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CORTEST

FINAL REPORT

ONR CONTRACT N00014-90-C-0100

Development of a Mathematical Model of Crevice Corrosion Propagation on Nickel Base Alloys in Natural and Chlorinated Sea Water

Author .... Date .....30 Aug '94.....

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Attn : Dr A. John Sedriks, Code 1131M

94-28875

Executive Summary

Crevice corrosion initiation and propagation of nickel base alloys Inconel 625, Hastelloy C276 and Hastelloy 22 in sea water and chlorinated sea water has been studied by exposure tests, electrochemical studies, surface analysis and mathematical modelling. The initiation of attack has been shown to be a function of crevice geometry and surface composition and has been successfully predicted by the modelling route. A mechanism of propagation has been suggested which successfully predicts large differences in the corrosion rate of Inconel 625 for relatively small changes in crevice geometry and temperature. This work is being further developed under the project expansion.

Contents

1. Introduction

Th ... e year project was scheduled to run from 1st April 1990 to 31st March
19 ... month, no funds extension was granted giving a completion date of 30th
Se...ember 1993. In 1992 a project expansion was awarded to run from 1st June
1992 to 31st December 1994 (ONR Contract N00014-92-C-0078). A 3 month, no
funds extension, extending this completion date to 31st March 1994 has been
requested.

The goal of the initial project was to establish the mechanism of crevice corrosion
propagation of corrosion resistant nickel base alloys in natural and chlorinated sea
water. Once established the mechanism was to be used to develop a mathematical
model of the process to allow predictions to be made indicating under what
conditions corrosion will occur and at what rate. This document is the final report of
the initial project. The full and detailed mathematical modelling has not been fully
completed within this project because of the continuing nature of the project
expansion. A model, meeting the goals of both the initial project and the expansion
will be part of the final repc ... the project expansion.

2. Background

The detailed background to this project is given in the proposal of March 1990
submitted to ONR (Dr A John Sedriks) by Cortest Laboratories Inc (now CLI
International Inc) of Houston, Texas. A copy of the 'as submitted document',
together with its covering letter, is presented in Appendix 1.

3. Results

Results obtained have been reported in Status Reports issued in July each year
throughout the project. Copies of these are given in Appendices 2-5 for 1990, 1991,
1992 and 1993 respectively.

The majority of the data reported in the status reports, together with the results of
additional studies carried out between July and September 1993 are described in a
paper 'Performance of Nickel Base Alloys in Critical Sea Water Applications' by J.
W. Oldfield which was presented and published at the NACE Corrosion Asia 94
Conference held in Singapore, September 1994. A copy of this paper is given in
Appendix 6.

4. Discussion

The discussion detailed in the paper in Appendix 6 represents the status of this
study at the completion of this project. As already noted, further studies have and
are being carried out under the project expansion which will result in the goals of
both projects being met.

5. Summary and Conclusions

Crevice corrosion initiation and propagation of nickel base alloys Inconel 625, Hastelloy C276 and Hastelloy 22 in sea water and chlorinated sea water has been studied by exposure tests, electrochemical studies, surface analysis and mathematical modelling. The initiation of attack has been shown to be a function of crevice geometry and surface composition and has been successfully predicted by the modelling route. A mechanism of propagation has been suggested which successfully predicts large differences in the corrosion rate of Inconel 625 for relatively small changes in crevice geometry and temperature. This work is being further developed under the project expansion.
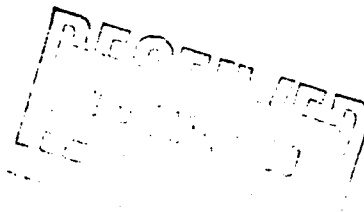
Appendix 1. Proposal Submitted to ONR.

March 9, 1990   L900809K

Dr. A. J. Sedriks
Office of Naval Research
800 Quincy Street
Code 1131
Arlington, Virginia 22217

DEVELOPMENT OF A MATHEMATICAL MODEL OF
CREVICE CORROSION PROPAGATION OF NICKEL
BASE ALLOYS IN NATURAL AND CHLORINATED SEA WATER

Dear Dr. Sedriks:

Enclosed please find three copies (one with original
signature) of Cortest's proposal to the Office of Naval
Research for the "Development of a Mathematical Model of
Crevice Corrosion Propagation of Nickel Base Alloys in
Natural and Chlorinated Sea Water".

The proposal has been written by Dr. John W. Oldfield of
Cortest Laboratories, Ltd., in the UK and if we are awarded
the contract to carry out the work, it will be subcontracted
by Cortest Laboratories, Inc., to Dr. Oldfield and will
commence April 1, 1990. I will act as the contract
negotiator and Dr. Oldfield will be the Principal
Investigator.

If you have any questions regarding the proposal, please do
not hesitate to contact me.

Best regards,

Dr. Russell D. Kane
President
Cortest Laboratories, Inc.

RDK/ac

Enclosures
RDK-2A/L900809K.CL

CORTEST
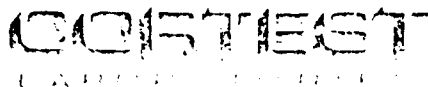
PROPOSAL FOR
DEVELOPMENT OF A MATHEMATICAL MODEL
OF CREVICE CORROSION PROPAGATION OF
NICKEL BASE ALLOYS IN NATURAL AND
CHLORINATED SEA WATER

PREPARED FOR:
OFFICE OF NAVAL RESEARCH
800 QUINCY STREET
CODE 1131
ARLINGTON, VIRGINIA 22217
ATTENTION: DR. A. JOHN SEDRIKS

PREPARED BY:
DR. JOHN W. OLDFIELD
CORTEST LABORATORIES, LTD.
23 SHEPHERD STREET
SHEFFIELD S3 7BA
YORKSHIRE, UK

DATE PREPARED: MARCH 9, 1990
CORTEST NO. : 900809K

INTRODUCTION

This proposal relates to a fundamental program of work to establish the mechanism of crevice corrosion propagation of corrosion resistant nickel base alloys in natural and chlorinated sea water. Once established, the mechanism will be used to develop a mathematical model of the process to allow predictions to be made indicating under what conditions corrosion will occur and at what rate.

The proposal is in two phases. Phase I, lasting 18 months, will establish the feasibility of developing such a model. This will include mechanistic investigations, the initiation of long term (1 to 2 years) exposure tests and development of an outline of the model. In Phase II, lasting 18 months, the model will be constructed, exposure tests to verify the model will be continued and detailed experimental data required by the model will be determined.

BACKGROUND

Mechanism of Crevice Corrosion in Natural Sea Water

The successful use of stainless steels and nickel base alloys in sea water depends to a large extent on their resistance to crevice corrosion. This form of attack typically occurs in shielded areas in bulk environments containing chloride ions.

The mechanism of crevice corrosion in natural sea water can be outlined as follows [1]:

1. Initiation
    - Deoxygenation of solution within a crevice
    - Development of an aggressive solution within the crevice, namely low pH and high Cl-

-1-

- Eventual breakdown of the passive film within the crevice.

2. Propagation
- "Active" corrosion within the crevice

During the initiation stage the passive current within the crevice is the anodic reaction while oxygen reduction, again within the crevice is the cathodic reaction. With time, oxygen within the crevice is depleted since it is reduced more quickly than it can be replaced by diffusion from the bulk solution. Once this occurs, the cathodic reaction moves outside the crevice and the anode and cathode of the cell are separated.

There are now mass transport considerations associated with the current between the anode and cathode. [2] in general terms, migrations lead to anions moving towards the anode and cations moving away from it, thus within the crevice there is a build up of anions from the bulk solution while some of the metal cations going into the solution via the passive current are driven out of the crevice. In addition, the overall increase in concentration of species within the crevice results in diffusion out of the crevice. For stainless steels and nickel base alloys the chromium ions which pass into the crevice solution via the passive current, hydrolyse and bring about a fall in the pH.

These processes, whereby an aggressive solution develops within the crevice, continue until either a steady state is reached where overall mass transport in and out of the crevice are equal, or the passive film on the alloy breaks down and propagation commences. Whether or not corrosion occurs can thus be seen to depend on the crevice geometry which controls the mass transport, the level of chromium in the alloy and the alloy's passive current which control the

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pH fall within the crevice, the chloride level of the bulk solution and the solution which will cause breakdown of the alloys passive film (this is usually termed the critical crevice solution (CCS) and is a high chloride, low pH solution which gives an active anodic peak on a polarization curve of typically 10uA/cm^2). [3]

Should propagation occur then the rate of attack can be limited by one of three factors, the anodic dissolution rate, the cathodic reaction rate or the IR potential drop between the anode and cathode.

Mathematical Modelling of Crevice Corrosion in Natural Sea Water

Mathematical modelling of the initiation stage of crevice corrosion of stainless steel and nickel base alloys in sea water and other chlorinated environments has been carried out previously. [2] This modelling is successful in that, with appropriate input parameters, e.g., CCS and passive current values, it predicts quite accurately whether or not corrosion will occur in a given situation.

A limited amount of work, mainly qualitative, has been carried out on the propagation of crevice corrosion. [4,5] To a large extent this has concentrated on explaining the difference between propagation rates in synthetic and natural sea water. Corrosion rates in natural sea water are typically an order of magnitude greater than synthetic sea water and this is attributed to the catalysis of the cathodic reaction, namely oxygen reduction in natural sea water.

Crevice Corrosion of Nickel Base Alloys in Sea Water

High molybdenum containing nickel base alloys are generally

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considered to have excellent resistance to crevice corrosion in sea water. This family of alloys is typified by Alloy 625, Alloy C276 and Alloy C22 with nominal compositions as given in Table 1.

In recent years, however, test results on some of these alloys have shown their resistance to fall somewhat short of what normally could be expected. In sea water [6,7] and other environments [8] initiation of attack has occurred quite readily. The cause of this phenomena has been attributed by some authors [8] to chromium depletion on the surface of the alloys whose metallurgy is extremely complex.

In sea water tests, particularly chlorinated sea water, the initiation of corrosion followed by extremely rapid propagation of attack was observed. [6] For example, in nat"ra! sea water Alloy 625 had a maximum depth of attack of 1.ᴊᴏmm in 360 days. In sea water chlorinated to ca 1ppm the maximum depth of attack was 0.51mm in 190 days and in highly chlorinated sea water, ca 90ppm, it was 2.31 in 60 days.

The relative ease of initiation of attack, even in unchlorinated sea water, can to some extent be explained by the conventional crevice corrosion mechanism taking account of crevice geometry and metallurgical considerations. The mechanism · of the rapid rate of propagation in both chlorinated and unchlorinated sea water is not understood.

This proposal sets out a program of work to confirm the mechanism of initiation of attack and to establish the mechanism of propagation. A mathematical model of the propagation of crevice corrosion will be developed to allow predictions to be made indicating under what conditions corrosion will occur and at what rate.

PROGRAM OF WORK - PHASE I

Mechanism of Initiation of Crevice Corrosion

Natural Sea Water

Electrochemical studies will be carried out to obtain values of the passive current and critical crevice solution (CCS) values for the three alloys listed in Table 1. Values will be used as input to Cortest's mathematical model of crevice corrosion initiation. [2] Results will be compared with exposure test data reported in the literature [6] and with data obtained from this project. Based on the comparison, the mechanism of initiation, including its dependence on surface finish, will be deduced.

Chlorinated Sea Water

Chlorination of sea water is a complex chemical process. The normal levels of chlorination used, namely less than 10ppm, result in the oxidation by chlorine of bromide in the sea water to bromine and hypobromous acid. [9] If ammonia is present, then bromamines and chloramines are formed and the processes become even more complicated. [10].

From the point of view of crevice corrosion initiation, the presence of a strong oxidizing agent is to increase the potential of the metal in the noble direction. The influence of this on the passive current and CCS values obtained in natural sea water will be determined from electrochemical studies. To complement these studies data will be generated to give the corrosion potential, prior to propagation of attack on the three alloys being studied, as a function of the level of chlorination.

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Another aspect of chlorination that may influence matters is the possible diffusion of oxidizing bromine compounds into the crevice which are then reduced to hydrobromic acid. The influence of this on the passive current and CCS values will be estimated.

Values of the passive current and CCS related to chlorination level via the appropriate corrosion potentials will be used as input to Cortest's mathematical model of crevice corrosion initiation. [2] As with natural sea water, results will be compared with exposure test data reported in the literature [6] and with data obtained from this project. Based on comparisons the mechanism of initiation will be deduced.

Crevice Corrosion Exposure Test Program

Natural Sea Water

Filtered sea water tests will be carried out at the Admiralty Research Establishment (ARE) at Holton Heath, Poole (UK). One matrix set as per Table 2 will be tested for two years in a tank which is continually refreshed with filtered sea water at ambient temperature. Additional samples of Alloy 625 will be included for removal after one year.

Chlorinated Sea Water

These tests will also be carried out at ARE. One matrix set as per Table 2 will be tested for two years in sea water with a 1ppm residual chlorine level. Again, tests will be carried out in a tank which is continually refreshed with chlorinated filtered sea water at ambient temperature. Additional samples of Alloy 625 will be included for removal after one year.

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Outline of Mathematical Model of Propagation

The propagation of crevice corrosion is an active electrochemical cell with the usual three components, an anodic reaction, a cathodic reaction and an IR potential drop between these. The mechanism of attack in a specific situation can be controlled by one of these components or by a combination of any two or all three. Small differences in circumstances can cause a switch of control from one mechanism to another. For example, at the start of propagation control may be the IR drop down the crevice whereas after a while the crevice gap may widen resulting in control by the cathodic reaction (if the external area is large for example) or by the anodic reaction (if the external area is small for example).

In natural sea water when propagation occurs the cathodic reaction is essentially oxygen reduction. The solution in the crevice has a low pH but it is unlikely that hydrogen evolution occurs to any great extent both because of the potential of these nickel base alloys and because if it does occur, it tends to be self limiting since it increases the pH by removing the H^+ ions.

The influence of chlorination on the mechanism of propagation is unknown. In principal, it can affect all three components of the electrochemical cell. Since it can change the potential of the specimen, it can influence the anodic dissolution rate. Since it is an oxidizing agent it clearly will influence the total cathodic reaction rate. Finally, it may effect the IR drop limitation on corrosion rate by virtue of supplying oxidizing agents to the crevice solution. This could occur since some of the bromine species may diffuse into the crevice. If this takes place, then part of the cathodic reaction occurs within the crevice and the product of that reaction is hydrobromic acid.

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Based on this view of the mechanism of propagation, the data and mechanism information relating to crevice corrosion initiation and the exposure test data available an outline of the model of crevice corrosion propagation of nickel base alloys in natural chlorinated sea water will be defined.

This will consist of a flow chart of the model identifying modelling work to be carried out, additional data to be obtained as input to the model and additional exposure test data required for satisfactory verification of the model.

PROGRAM OF WORK - PHASE II

Mathematical Modelling

The model outlined as a result of Phase I will be developed. It will take as a starting point the breakdown conditions predicted by Cortest's model of crevice corrosion initiation, taking account of any modification required as a result of data generated in Phase I.

The model will be in three parts corresponding to the three possible controlling mechanisms, anodic, cathodic or IR. The interaction of these mechanisms will also be taken into account. This aspect of the model will be the most complex. The influence of the level of chlorination will be built into the model.

Mechanistic and Other Data Required
for the Mathematical Model

Crevice Corrosion Propagation in Natural Sea Water

Electrochemical studies will be carried out on the active dissolution of the three alloys in Table 1 to establish their maximum dissolution rates as a function of potential and crevice solution composition.

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Data on the cathodic reduction of oxygen on nickel-base alloys in sea water will be sought from the literature. Some data will be generated as part of this project to complement what is found in the literature. From the estimates of the maximum cathodic current densities that can exist under different circumstances will be estimated.

Calculations will be made on the influence of crevice geometry on the propagation process by way of the IR potential drop down the crevice. Considerations will be given to the influence of corrosion product on the IR potential drop between anode and cathode.

Crevice Corrosion Propagation in Chlorinated Sea Water

Electrochemical studies will be carried out to establish the effect, if any, of additions of hydrobromic acid to low pH high chloride solutions. This effect will be quantified in terms of maximum anodic corrosion rates and compared with values in solutions that develop in crevices in natural sea water alone.

Data on the cathodic reduction of hypobromous acid and hypobromite on nickel base alloys in sea water will be sought from the literature. Some data will be generated as part of this project to complement what is found in the literature. From these estimates of the maximum cathodic current densities (oxygen reduction and the reduction of bromine and its compounds) will be made.

Other Data

The data obtained in Phase I during the mechanistic studies together with that referred to in the abovementioned paragraphs will be required as input data for the mathematical model. However, much additional data will also

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be required relating to equilibrium constants, diffusion constants, mobilities, etc., for species present, including those resulting from the chlorination process. These data will be obtained from the literature and collated.

Verification and Use of the Mathematical Model

Predictions of the mathematical model will be verified by comparison with the exposure test results obtained. Modifications to the model may be required as this stage.

The outcome of this task will be a mathematical model, with clear definitions of the scope of its use and its limitations, which can predict the crevice corrosion propagation performance of nickel base alloys in natural and chlorinated sea water. The basis of the model will be the result of mechanistic study of crevice corrosion propagation.

TIMESCALE

The timescale for the overall project is summarized in Figure 1 where tasks are identified by their numbers given in Table 3.

Phase I is over the first 18 months of the three year program and Phase II is over the second 18 months.

The project is scheduled to commence April 1, 1990.

COST AND SPEND SCHEDULE

The overall cost of the program of work is as follows:

Phase I	$ 73,315.00
Phase II	$102,729.00
TOTAL	$176,044.00

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The estimated number of hours required to complete each task is detailed in Table 4.

Detailed breakdowns of the costs for Phase I and Phase II are given in Tables 5 and 6, respectively. In calculating these costs current rates in pounds sterling have been converted to US dollars using the present exchange rate of $1.67/pound sterling. Inflation has been assumed at 8 percent which is slightly less than the currently prevailing rate in the UK. An average hourly rate over each Phase (18 months) has been calculated. Fees have been taken at 10 percent of the direct labor cost.

REPORTING

Status reports will be issued at 9, 18 and 27 months with a final report upon completion of the project.

Prepared by: _____   Date: March 9, 1990
Dr. John W. Oldfield
Director

Reviewed by: _____   Date: March 6, 1990
Mr. James A. Madigan
Manager, Business Development

RDK-2B/900809K.P

REFERENCES

1.   Fontana, M.G., & Green, N.D., Corrosion Engineering, p41, McGraw Hill, New York, 1967.

2.   Oldfield, J.W., & Sutton, W.H., Br. Corros. J. 13, 13 (1978).

3.   Oldfield, J.W. & Sutton, W.H., Br. Corros. J. 15, 31 (1980).

4.   Oldfield, J.W., Lee, T.S., & Kain, R.M., "Proc. Int. Symp Corr & Prot, 160th Electrochem. Soc. Meeting, Denver, Oct. 1981, p213.

5.   Oldfield, J.W., Lee, T.S., & Kain, R.M., "Proc. Chem, within Pits, Crevices and Cracks, NPL, Oct. 1984, Ed. A Turnbull, p89.

6.   Kain, R.M., Ferrara, R.J., & Shaw, B.A., NACE CORROSION/89, Paper 112, New Orleans.

7.   Thomas, E.D., Lucas, K.E., Peterson, M.H. & Christian, D.K., NACE CORROSION/88, Paper 402, St. Louis.

8.   Dille, E.R., McDonald, J.I., & Berry, P., NACE CORROSION/88, Paper 8, St. Louis.

9.   Oldfield, J.W., & Todd, B., Desalination, 38, 233 (1981).

10. Lee, W.S., Oldfield, J.W., & Todd, B., Desalination 44, 209, (1983).

TABLE 1
Chemical Composition of Materials (Nominal) W%

Mat.	Ni	Cr	Mo	C	Fe	Other
Alloy 625 (1)	58.0 min	20.0-23.0	8.0-10	0.10 max	5.0 max	3.2-4.2 Cb+Ta 1.0 Ti max 1.0 Co max
Alloy C-276 (2)	Bal	14.5-16.5	15.0-17.0	0.02 max	4.0-7.0	3.0-4.5 W 1.0 Co max
Alloy C-22 (2)	Bal	20.0-22.5	12.5-13.5	0.015 max	2.0-6.0	2.5-3.5 W 2.5 Co max

(1) Alloy 625 supplied by Huntington Alloys, West Virginia, USA.

(2) Alloys C-276 and C-22 supplied by Haynes International, Manchester, UK.

TABLE 2
Crevice Corrosion Exposure Test Matrix

Materials: Alloy 625, Alloy C-276, Alloy C-22

Surface Finish: Pickled (as received), ground

Crevice Geometry: 5mm annulus Perspex crevice former
                    direct onto specimen, same but with
                    vinyl washer between Perspex and
                    crevice former

Samples: Duplicate

TABLE 3
Task Identification

PHASE I

1. Mechanism of Initiation of Crevice Corrosion

    1.1 Natural Sea water
    1.2 Chlorinated Sea Water

2. Crevice Corrosion Exposure Test Program

    2.2 Natural Sea Water
    2.2 Chlorinated Sea Water

3. Outline of Mathematical Model of Propagation

PHASE II

4. Mathematical Modelling

5. Mechanistic and Other Data Required for the
    Mathematical Model

    5.1 Crevice Corrosion Propagation in Natural Sea Water

    5.2 Crevice Corrosion Propagation in Chlorinated Sea
         Water

    5.3 Other Data

6. Verification and Use of the Mathematical Model

TABLE 4
Estimated Hours to Complete Each Task

Phase I

Task Number	Principal Engineer	Senior Technician
1.1	22.5	150.0
1.2	37.5	150.0
2.1	15.0	67.5
2.2	15.0	67.5
3	112.5	-----
	202.5	435.0

Phase II

Task Number	Principal Engineer	Senior Technician
4	150.0	-----
5.1	82.5	225.0
5.2	60.0	225.0
5.3	37.5	-----
2.1	-----	21.5
2.2	-----	21.5
6	150.0	-----
	480.0	493.0

TABLE 5
Cost Breakdown for Phase I (U.S. Dollars)

Direct Labor

Principal Investigator - 202.5 hours @ $86/hour	$17,415	
Senior Technician - 435 hours @ $50/hour	$21,750	
Total Direct Labor		$39,165

Direct Material

Metal	$ 1,500	
Chemicals	$ 2,165	
Machining - 64 samples @ $67/each	$ 4,299	
Total Direct Material	$ 7,953	
Total Direct Material X Overhead Rate (0.10)		$ 8,748

Travel

Transportation - 1 trip to ONR	$ 1,250	
- 8 trips to APE @ $240/each	$ 1,920	
Per Diem Costs - 13 days @ $135/each	$ 1,755	
Total Travel Costs		$ 4,925

Equipment Use

Computer - 300 hours at $5/hour	$ 1,500	
Exposure Test Equipment - 15 months @ $420/month	$ 6,300	
ARE Laboratory Facilities	$ 6,012	
Total Equipment Use		$13,812
Total Excluding Fees		$66,650
Fees (10 percent)		$ 6,665
GRAND TOTAL FOR PHASE I		$73,315

TABLE 6
Cost Breakdown for Phase II (U. S. Dollars)

Direct Labor

Principal Investigator - 480 hours @ $97/hour	$46,560	
Senior Technician - 493 hours @ $67/hour	$28,101	
Total Direct Labor		$ 74,661

Direct Material

Chemicals	$ 2,165	
Total Direct Materials	$ 2,165	
Total Direct Materials X Overhead Rate (0.10)		$ 2,382

Travel

Transportation - 1 Trip to ONR	$ 1,420	
- 8 Trips to ARE @ $267/each	$ 2,136	
Per Diem Costs - 13 Days @ $150/each	$ 1,950	
Total Travel Costs		$ 5,506

Equipment Use

Computer - 300 hours @ $5/hour	$ 1,500	
Exposure Test Equipment - 9 months @ $420/month	$ 3,780	
ARE Laboratory Facilities	$ 5,561	
Total Equipment Use		$ 10,841

Total Excluding Fees	$ 93,390
Fees (10 percent)	$ 9,339
GRAND TOTAL FOR PHASE II	$102,729

Task (See Table 3)	Year 1				Year 2				Year 3			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	A4
Phase I												
1.1	--											
1.2		--										
2.1	---											
2.2	---											
3						--						
Phase II												
4						-------------------						
5.1						--------						
5.2								--------				
5.3							--					
6										---------		

Figure 1
Timescale

APPENDIX I

BIOSKETCH OF:
DR. JOHN W. OLDFIELD

JOHN W. OLDFIELD

Dr. Oldfield is currently Managing Director of Cortest Laboratories Ltd, Sheffield, UK. In this capacity he is involved with corrosion testing, research and consulting specializing in the use of stainless steels and nickel base alloys.

Prior to joining Cortest in 1987, Dr. Oldfield held the position of Vice President of Inco's Middle East Projects Group and was Technical Service Manager of Inco Engineered Products, Ltd., operating out of Birmingham, UK.

Dr. Oldfield spent 1967 through 1970 as a Research Fellow to the Department of Electrochemistry, Southampton University, working with Professor Martin Fleischmann. In 1970 he joined Inco's European Research & Development Centre where he gained much experience in practical corrosion problems to complement his electrochemistry/mathematical background. In 1980 he was made Deputy Manager of the Electrochemical Group.

In 1982 he was seconded for one year to Inco Alloys International in Hereford, UK as Industry Manager for their Alloy Marketing Group and was responsible for developing markets and handling corrosion problems for nickel base materials in the offshore and chemical process industries. On his return, Dr. Oldfield was named General Manager, Technology, of Inco's Middle East Projects Group. This group operated a corrosion consulting business with offices in Bahrain. A major effort of the group was technical corrosion support of the design, construction and operation of desalination plants for the Saudi Arabia Saline Water Conversion Corporation (SWCC) over a period of six years (1980 - 1986).

From 1986 through 1989, Dr. Oldfield was Chairman of the Society of Chemical Industries Materials Preservation Group (UK) and is currently Chairman of the Corrosion Engineering Association Task Group on Materials Selection for Oil and Gas Production.

Education

B.Sc., Physics and Chemistry (1963)
University of Newcastle

Ph.D., Electrochemistry (1967)
University of Newcastle

-1-

Publications

1. R. D. Armstrong, M. Fleischmann and J. W. Oldfield, "The Anodic Formation of Phosphates of Mercury", J. Electroanal Chem, 14, 1967, 235.

2. R. D. Armstrong, M. Fleischmann and J. W. Oldfield, "Properties of Anodically Formed Mercury-Barbiturates", Trans Farad, Soc. 65 1969, 3053.

3. M. Fleischmann and J. W. Oldfield, "Mass Transfer Problems and Polarization in Fluidized Bed Electrodes", Society for Electrochemistry Electrode Polarization Colloquium, Brighton, December 11-12, 1969, p. 14.

4. M. Fleischmann and J. W. Oldfield, "Generation-Recombination Noise in Weak Electrolyte", J. Electroanal Chem. 27, 1970, 207.

5. J. R. Backhurst, F. Goodridge, M. Fleischmann and J. W. Oldfield, "Improvements in and Relating to Electrochemical Cells", British Patent No.: 2148402 (Applic. N. 45999/70, September 28, 1970).

6. M. Fleischmann and J. W. Oldfield, "Fluidized Bed Electrodes Part I. Polarization Predicted by Simplified Models", J. Electroanal Chem, 29, 1971, 211.

7. Mr. Fleischmann and J. W. Oldfield, "Fluidized Bed Electrodes Part II, The Effect Resistivity of the Discontinuous Metal Phase". J. Electroanal Chem, 29, 1971, 231.

8. M. Fleischmann, J. W. Oldfield and D. F. Porter, "Fluidized Bed Electrodes, Part III, The Cathodic Reduction of Oxygen on Silver in a Fluidized Bed Electrode", J. Electroanal. Chem. 29, 1971, 241.

9. Mr. Fleischmann, J. W. Oldfield and L. Tennakoon, "Fluidized Bed Electrodes, Part IV, Electrodeposition of Copper in a Fluidized Bed of Copper Spheres', J. Appl. Electrochem 1, 1971, 103.

10. M. Fleischmann, J. W. Oldfield and C. L. K. Tennakoon, "The Bipolar Particulate Cell", Symposium on Electrochem. Eng. Newcastle, March 1971, Vol I, p. 63.

11. M. Fleischmann, C. J. H. King, J. W. Oldfield, R. E. Plumley and L. K. Charles, "Improvements in and Relating to Electrochemical Cells', British Patent No.: 2262166 (Applic. No. 60763/71, December 30, 1971).

12. P. Bindra, M. Fleischmann, J. W. Oldfield and D. Singleton, "Nucleation", Farad. Disc. No. 56, 1973, p. 180.

-2-

13. J. W. Oldfield, "The Use of Computer Simulations to Study the Nature of an Electrodeposit during the Early Stages of Growth", Electrodep. Surf. Tr. 2, 1972, 74, 395.

14. J. W. Oldfield and W. H. Sutton, "Crevice Corrosion of Stainless Steels', 6th European Cong. on Corrosion, London 1977, p.239.

15. J. W. Oldfield and W. H. Sutton, "Crevice Corrosion of Stainless Steels. I. A. Mathematical Model", Brit. Corros J. 13(1), 1978, 13.

16. J. W. Oldfield and W. H. Sutton, Crevice Corrosion of Stainless Steels - Predicted Effects of Geometry on Crevice Corrosion Susceptibility". 153rd Electrochem. Soc. Meeting, Seattle, 1978, extended abstract 69.

17. J. W. Oldfield and W. H. Sutton, "Crevice Corrosion of Stainless Steels, II. Experimental Studies, Brit. Corros. J. 13(2), 1978, 103.

18. J. W. Oldfield, W. H. Sutton and G. L. Swales, "A New Technique for Predicting the Performance of Stainless Steels in Sea Water", ME-NACE Corros. Conf., Bahrain, April 1979.

19. J. W. Oldfield and W. H. Sutton, "A New Technique for Predicting the Performance of Stainless Steels in Sea Water and Other Chloride Containing Environments", Brit. Corros. J. 15 (1), 1980, 31.

20. J. W. Oldfield and B. Todd, "Corrosion Consideration in Selecting Metals for Flash Chambers", Desalination, 31, 1979, 365.

21. J. W. Oldfield, "Crevice Corrosion of Stainless Steels - The Importance of Crevice Geometry and Alloy Composition", 19th Journees des Aciers Speciaux, St. Etienne, May 1980. Paper 19.

22. J. W. Oldfield, M. Turner and T. S. Turner, "The Behavior of CMG Positive Electrodes in Nickel Cadmium Cells", Power Sources 8, Ed. J. Thompson, Academic Press 1981, p. 427.

23. J. W. Oldfield, G. L. Swales and B. Todd, "Corrosion of Metals in Deaerated Seawater", Proc. 2nd BSE-NACE Corr. Conf., Bahrain, Jan 1981, p. 48.

24. J. W. Oldfield, R. M. Kain and T. S. Lee, "A Mathematical Model of Crevice Corrosion Propagation of Stainless Steels", Corrosion/81, Corrosion Research Conference, Localized Corrosion Session, Toronto, April 1981 (Abstract only).

25. J. W. Oldfield, "Crevice Corrosion of Stainless Steels - The Importance of Crevice Geometry and Alloy Composition:, Metauz Corrosion-Industrie, April 1981, No. 668, p. 134.

26. J. W. Oldfield and T. S. Turner, "Mathematical Model of a CMG Nickel Hydroxide Electrode", 159th Electrochem, Soc. Meeting, Minneapolis, May 1981, Extended Abstract No. 6, p.20.

27. J. W. Oldfield, T. S. Lee and R. M. Kain, "Mathematical Modelling of Crevice Corrosion of Stainless Steels", Proc. Int. Symp. Corr. and Prot., 160th Electrochem Soc. Meeting, Denver, October, 1981, p. 213.

28. J. W. Oldfield and B. Todd, "The Use of Stainless Steels in MSF Desalination Plants", Arab Water Technology Conf. Dubai, UAE, November, 1981.

29. J. W. Oldfield and B. Todd, "Corrosion Problems Caused by Bromine Formation in MSF Desalination Plants", Desalination 38, 1981, 233.

30. J. W. Oldfield, T. S. Lee and R. M. Kain, "Mathematical Modelling of the Initiation and Propagation Stages of Crevice Corrosion on Stainless Steels", Electrochem Methods in Corr. Testing and Research Conf., UMIST, January 1982 (Abstract only).

31. T. S. Lee, J. W. Oldfield, R. M. Kain and C. S. O'Dell, "Assessing Crevice Corrosion Behavior of Stainless Steels in Natural Waters via Mathematical Modelling", Corrosion/82, Corrosion Research Symposium, Houston, March 1982 (Abstract only).

32. J. W. Oldfield, "Mathematical Modelling of Crevice Corrosion of Stainless Steels", Gordon Research Conf., July 26-30, 1982, New London, NH, USA (Presentation only).

33. T. S. Turner, D. M. Tallett, J. W. Oldfield and J. Edwards, "The Performance of CMG Nickel Hydroxide Electrodes as a Function of their Structure", 13th International Powder Sources Symposium, Brighton, September, 1982.

34. T. S. Lee, J. W. Oldfield, and R. M. Kain, "The Role of Oxygen Reduction in Crevice Corrosion", 162 Electrochem. Soc. Meeting, Detroit, October 17-22, 1982 (extended Abstract).

35. B. Todd and J. W. Oldfield, "Stainless Steel Corrosion Caused by Bromine Formation in MSF Desalination Plants", Proc. UK National Corrosion Conf., November 16-18, 1982, London, p. 77.

-4-

36. T. S. Lee, R. M. Kain and J. W. Oldfield, "The Influence of Environmental Variables on Crevice Corrosion of Stainless Steels", Corrosion/83, Corrosion Research Symposium, Anaheim, California, April 1983.

37. W. S. W. Lee, J. W. Oldfield and B. Todd, "Corrosion Problems Caused by Bromine Formation in Additive Dosed MSF Plants", 1st World Congress on Desalination and Water Re-Use, Florence, May 1983.

38. J. W. Oldfield, "The Use of Computers in Predicting the Corrosion Resistance of Stainless Steels", 24th Corrosion Science Symposium, Cambridge, September 13-16, 1983, (Abstract only).

39. J. W. Oldfield, "High Nickel Alloys for Offshore Applications", Advanced Corrosion Resistant Steels and Metals and Metal Alloys for Offshore Applications Conference, NITO, January 1984, Oslo and June 1984 Stavanger, Paper.

40. J. W. Oldfield, "Hot Riser Protection - Using Monel Alloy 400", Offshore Riser Protection - A Continuing Problem? Conference, I Corr S&T, London, Mary 8, 1984 (Presentation only).

41. J. W. Oldfield, T. S. Lee and R. M. Kain, " Avoiding Crevice Corrosion of Stainless Steels", Stainless Steels '84, September 1984, Gothenburg, Institute of Metals, 1985, p. 205.

42. J. W. Oldfield, T. S. Lee and R. M. Kain, "The Role of Oxygen Reduction and Hydrogen Evolution in Crevice Corrosion of Stainless Steels", Corrosion Chemistry within Pits, Crevices and Cracks, Conference, NPL, October 1-3, 1984.

43. J. W. Oldfield and B. Todd, "The Use of Stainless Steels and Related Alloys in Reverse Osmosis Desalination Plants", International Maritime Engineering Conference, Bahrain, October 21-25, 1984, Trans I Mar E (C) Vol. 97, p. 139.

44. J. W. Oldfield and B. Todd, "The Use of Stainless Steels and Related Alloys in Reverse Osmosis Desalination Plants", Proceedings of 2nd World Congress on Desalination and Water Reuse, November 17-22, Bermuda, Vol. 2, p. 261.

45. M. D. Carpenter, R. Francis, L. M. Phillips and J. W. Oldfield, "Electrochemical Tests to Assess Resistance to Crevice Corrosion in Sea Water of Some Duplex Stainless Steels", Br. Corros. J. 1986 <u>21</u> (1), 1986, 45.

46. B. Todd and J. W. Oldfield, "Corrosion Problems Caused by Chlorination in the Desalination Industry", SCI Materials Preservation Group Conf, March 4, 1986, Birmingham, Paper 4.

47. J. W. Oldfield, "Fundamental Aspects of Stainless Steels", Council of Europe Intensive Course on Prevention of Corrosion Hazards in Food Engineering, September 8-12, 1986.

48. J.W. Oldfield and B. Todd, "Reverse Osmosis - Which Stainess Steel to Use", Middle East Water and Sewage, October, 1986, Vol. 10. No. 5.

49. J. W. Oldfield, "Electrochemical Theory of Galvanic Corrosion", ASTM Symposium on Galvanic Corrosion, November 3-4, 1986, Phoenix.

50. S. Zaharani, B. Todd and J. W. Oldfield, "Bimetallic Joints in Multi-Stage Flash Desalination Plants" ASTM Symposium on Galvanic Corrosion, November 3-4, 1986, Phoenix.

51. J. W. Oldfield, "Review of Test Techniques for Pitting and Crevice Corrosion Resistance of Stainless Steels in Nickel Base Alloys in Chloride Containing Environments", International Metal Reviews, Vol. 32, No. 3. p 153, 1987.

52. J. W. Oldfield, "Corrosion Resistance of Stainless Steels", Welding Institute Seminar, Stainless Steels - Recent Developments in Materials and Welding, Coventry, December 3, 1986.

53. S.M. Wilhelm and J. W. Oldfield, "Effect of Elemental Sulfur on the Performance of Incoloy 825 in Deep Sour Gas Well Production", Proc. of 2nd International Conference on Sour Service in the Oil, Gas and Petrochemical Industries, London, May 11-12, 1987.

54. J. W. Oldfield and B. Todd, "Vapor-Side Corrosion in MSF Plants", 3rd World Congress on Desalination and Water Reuse, Cannes, September 14-17, 1987, Desalination 66 (1987), 171-184.

55. J. W. Oldfield, "Crevice Corrosion of Stainless Steels in Sea Water", 10th ICMC Madras, November 7-11, 1987, B. Electrochem 3(6) 1987, p 599.

56. J.W. Oldfield, "Crevice Corrosion Resistance of Commercial and High Purity Experimental Stainless Steels in Marine Environments - The Influence of N, Mn and S", NACE CORROSION/88, Paper No. 409, St. Louis, March, 1988.

57. J. W. Oldfield, "Crevice Corrosion Resistance of Stainless Steels in Marine Environments: The Influence of N, Mn and S", Materials Performance, Vol. 27, No. 7, July, 1988.

58. J. W. Oldfield, "Crevice Corrosion of Stainless Steels in Seawater", Avesta Corrosion Management No. 1, 1988.

59. J. W. Oldfield, "Review of Materials for Sour Service", UK CORROSION/88, October 3-5, 1988, Brighton, Vol. 1, p321.

60. R. D. Kane and J. W. Oldfield, "Environmental Effects on Advanced Materials", Proc. of Aerospace Corrosion Control Conference, February 28 - March 2, 1989, Gleneagles, Organizer Sawell Publications, Ltd.

61. R. D. Kane, S. M. Wilhelm and J. W. Oldfield, "Review of Hydrogen Induced Cracking of Steels in Wet H_2S Refinery Service", Proc. International Conference on Interaction of Steels with Hydrogen in Petroleum Industry Pressure Vessel Service, March 28-30, 1989, Paris, Organizers MPC, Inc.

62. J. W. Oldfield, "Effect of Crevice Geometry on the Corrosion of AISI 304 and 316 in Marine Environments", NACE CORROSION/89, Paper No. 290. New Orleans.

63. J. W. Oldfield and R. M. Kain, "Assessment of the Corrosion Resistance of Austenitic Stainless Steels in Industrial Waters", 11th ICC, Florence, April 2-6, 1990.

64. R. M. Kain and J. W. Oldfield, "Crevice Corrosion Behaviour of Stainless Steels in Chloride and Sulfate Containing Waters", NACE CORROSION/90, Las Vegas, April 23-27, 1990.

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MARCH, 1990

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Appendix 2.   Status Report : July 1990.

CORTEST
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23 Shepherd Street, Sheffield. S3 7BA, UK.

STATUS REPORT – CONTRACT N00014-90-C-0100

DEVELOPMENT OF A MATHEMATICAL MODEL OF CREVICE CORROSION PROPAGATION OF NICKEL BASE ALLOYS IN NATURAL AND CHLORINATED SEAWATER

This 3 year contract commenced on 1st April 1990. The current status of the work is summarised below.

Mechanism of Initiation of Crevice Corrosion (TASK 1.1)

Electrochemical tests to determine passive current and critical crevice solution values for Inconel alloy 625 have been carried out in chlorine free synthetic sea water. Hastelloy C-22 and C- 276 material has been procured and testing on these materials will commence shortly.

Crevice Corrosion Exposure Test Program (TASKS 2.1 and 2.2)

Inconel alloy 625 samples have been prcured and prepared for exposure testing. Hastelloy C-22 and C-276 samples are expected shortly. Exposure test equipment for use at ARE, Holton Heath, Poole, UK has been designed, procured and commissioned at Cortest in Sheffield. Installation of the equipment and commencement of exposure tests is expected during August.

J.W.Oldfield

31 July 1990

Appendix 3. Status Report : July 1991.

Contract Title: Development of a Mathematical Model of Crevice Corrosion Propagation of Nickel Base Alloys in Natural and Chlorinated Sea Water.

Project Goals: To establish the mechanism of crevice corrosion resistant nickel base alloys in natural and chlorinated sea water. Once established the mechanism will be used to develop a mathematical model of the process to allow predictions to be made indicating under what conditions corrosion will occur and at what rate.

Present Status

Phase I (April 1 1990 to 30th Sept 1991)

Mechanism of Initiation of Crevice Corrosion (Tasks 1.1 and 1.2)

The composition of the major alloying elements in the three nickel base alloys studied in this project are as follows:-

Alloy	Cr	Ni	Mo	Fe
Inconel Alloy 625	22.3	60.0	8.82	4.47
Hastelloy C22	21.4	55.3(bal)	13.9	4.2
Hastelloy C276	15.4	57.1(bal)	16.0	5.89

Electrochemical tests to determine critical crevice solution values and passive currents for these three alloys have been carried out. Passive current values have been measured as a function of time. Values of this current after 100 hrs are given in Table 1. Critical crevice solution values and crevice corrosion resistance (CCR) values predicted by the mathematical model of crevice corrosion initiation are given in Table 2. In determining the CCR values the same passive current value was used for all three alloys.

Corrosion potentials have been measured in synthetic sea water with and without chlorine additions. Values obtained are summarised in Table 3.

CCS values show Inconel alloy 625 to be significantly inferior to the Hastelloy materials. The passive current values coupled with the corrosion potentials of the different alloys allow us to estimate the passive current relevant to each alloy in synthetic sea water. In unchlorinated sea water pickled and

passivated material behaves in a similar manner: ground material has potentials more noble by between 40 and 200mV. Inconel alloy 625 has corrosion potentials more noble than the Hastelloy materials by about 100mV in the case of pickled and passivated surfaces and 230mV in the case of ground material.

A preliminary analysis of the data shows that the corrosion potential difference between '625' and 'C22' results in similar passive currents being operative. The passive current value for 'C276' appears higher, due probably to its lower chromium content. At this stage of the Project the CCR values given in Table 2 for '625' and 'C22' are considered accurate while the value for 'C276' is considered high since no account was taken of its higher passive current in obtaining this data.

Corrosion potentials in chlorinated sea water show potentials going more noble as the chlorine level increases. Also at the lower chlorine levels there is a tendency for the potential to increase on going from 'C276' to 'C22' to '625'. From Table 1 we see that the passive current increases only moderately as the potential is increased from -200 to +300 mV. Between 300 and 400 mV however it increases by an order of magnitude. The resistance to crevice corrosion initiation under these conditions, which prevail in chlorinated sea water (see Table 3) will be severely reduced. In 1ppm chlorine this effect is more severe with '625' (350 mV) than with 'C22' (325 mV) and 'C276' (275 mV).

Results to date have quantified some of the differences in resistance to crevice corrosion initiation of the three alloys being tested in sea water and chlorinated sea water. Further analysis of the data is in progress.

Crevice Corrosion Exposure Test Programme (Tasks 2.1 and 2.2)

Samples of the three nickel base alloys have been procured and a 2-year test programme commenced in August 1990 at the Admiralty Research Establishment in Poole, UK where natural sea water is available. The exposure test rigs were designed. build and commissioned by Cortest as part of this Project.

Tests are being carried out in unchlorinated filtered sea water and chlorinated filtered sea water (1 ppm). Material is being tested in the as received condition and the ground condition. The crevice former is the 'Perspex' crevice annulus (5mm) used by Cortest and LCCT for a number of years. Two crevice geometries are being studied. with and without a PVC insert in the crevice. Results based on visual examination of the tests in situ are given in Table 4. Note that half the '625' samples are to be removed after 1 year (August 1991). These visual

data appear to indicate the superiority of 'C22' over '625' and in fact over 'C276'. The latter fact may well be linked with the low chromium and high passive current values of 'C276'. The severity of a PVC type crevice over a simple Perspex one is also highlighted.

Outline of Mathematical Model of Propagation (Task 3)

Work has commenced on this task but is at an early stage. The model of initiation and the interplay of CCS data and passive current with corrosion potentials appear, at this stage, to relate well to the preliminary results of th exposure test data.

Aspects of propagation which are currently being considered are the influence of high concentrations of nickel ions in the vicinity of the crevice once propagation has commenced. The usual considerations for propagation of stainless steels are those of high concentrations of ferrous ions. Nickel oxide is for example well known as a catalyst for oxygen reduction. It may be possible for such species to form either inside or outside the crevice and accelerated the rate of propagation.

This outline will be complete prior to the start of Phase II on the Project in October 1991.

Table 1   Passive Current Values at 100 hrs (uA/cm^2)

Surface Finish	Potential Vs SCE	C276	C22	625
passivated	500	3.0	7.0	3.6
"	400	1.2	1.4	1.1
"	300	0.11	0.11	0.04
"	200	0.10	0.07	0.04
"	0	0.08	0.05	0.03
"	-200	0.08	0.03	0.01
ground	200	0.10	0.11	0.03
"	0	0.08	0.08	0.02
"	-200	0.06	0.07	0.01
pickled	200	0.13	0.10	0.04
"	0	0.10	0.09	0.04
"	-200	0.08	0.06	0.01

Table 2   CCS Crevice Corrosion Resistance (CCR) Values

	CCS, pH (Cl$^-$=6N)	CCR
625	-0.27	2150
C22	-0.53	2630
C276	-0.59	2975

Table 3 Corrosion Potentials (vs SCE)

Environment	Surface Finish	C276	C22	625
Synthetic sea water	pickled	−235	−232	−120
"	ground	−194	−142	+ 92
"	passivated	−236	−238	−130
Synthetic sea water plus 1ppm Cl_2	passivated	275	325	350
Synthetic sea water plus 3ppm Cl_2	passivated	320	340	353
	ground	315	340	355
	pickled	355	370	385
Synthetic sea water plus 10ppm Cl_2	passivated	410	420	410

Table 4 Corrosion Sites Initiated 10 months into the
Exposure Test Programme (Total No of sites,
assuming 2 per specimen i.e. 1 either side)

Alloy	Crevice	Surface Finish	Sea Water	Chlorinated Sea Water
625	insert	Pickled	6 of 8	4 of 8
"	No insert	"	0 of 8	0 of 8
"	insert	Ground	0 of 8	0 of 8
"	No insert	"	1 of 8	0 of 8
C22	insert	CR Annealed	0 of 4	0 of 4
"	No insert	"	0 of 4	0 of 4
"	insert	Ground	0 of 4	0 of 4
"	No insert	"	0 of 4	0 of 4
C276	insert	CR Annealed	4 of 4	4 of 4
"	No insert	"	0 of 4	0 of 4
"	insert	Ground	4 of 4	2 of 4
"	No insert	"	0 of 4	0 of 4

Appendix 4. Status Report : July 1992.

ONR Contract N 00014-90-C-0100 Status Report at 1st July 1992

Contract Title: Development of a Mathematical Model of Crevice Corrosion Propagation on Nickel Base Alloys in Natural and Chlorinated Sea Water.

Project Goals: To establish the mechanism of crevice corrosion propagation of corrosion resistant nickel base alloys in natural and chlorinated sea water. Once established the mechanism will be used to develop a mathematical model of the process to allow predictions to be made indicating under what conditions corrosion will occur and at what rate.

Present Status

Phase I (April 1st 1990 - 30th Sept 1991)

Mechanism of Initiation of Crevice Corrosion (Tasks 1.1 & 1.2)

These tasks have been completed. It is concluded that initiation of attack in both chlorinated and unchlorinated sea water is by an acidification-depassivation mechanism. Surface finish is an influencing factor on Inconel alloy 625, a pickled surface being more prone to attack than a ground surface. The passive current appears similar on both surfaces but there are indications that in chlorinated sea water the potential on pickled material is more noble than on ground material. Crevice geometry is important, as demonstrated by exposure test results (see below).

Crevice Corrosion Exposure Test Programme (Tasks 2.1 & 2.2)

That part of these tasks scheduled for Phase I have been completed. A full set of Inconel alloy 625 samples were removed from test after 1 year in August 1991. These were duplicate samples of ground and pickled samples with Perspex* and Perspex plus a vinyl insert assemblies, all tested in natural sea water and natural sea water chlorinated to 1ppm residual chlorine i.e. 16 samples in all. A summary of observations on these samples is given in Table 1. Corrosion occurred on one side of 4 samples, initiating by 21 days (observations were made every 2-3 days) on all 4 pickled samples with the assemblies containing the vinyl inserts. Attack was superficial with no significant depth of attack. Clearly the pickled surface is more prone to attack than the ground surface and the crevice with the vinyl insert is more

* Trademark

severe than the Perspex crevice. There appears to be little difference in the severity of chlorinated and unchlorinated sea water at the level of chlorination used. (1 ppm residual).

Outline of Mathematical Model of Propagation (Task 3)

The outline of the model of propagation has now been completed. It assumes that initiation of corrosion is by acidification and breakdown of the protective film via the generally accepted mechanism for crevice corrosion of stainless steels. The time to breakdown is influenced by the crevice geometry and environment, the latter influencing both the passive current and critical crevice solution (CCS) value. Chlorination and natural sea water result in a range of corrosion potentials which can influence the passive current; chlorination itself does not influence the CCS value.

The propagation rate can be controlled by either the anodic dissolution of the metal (anodic control), the cathodic process, usually oxygen reduction (cathodic control) or by the IR potential drop down the crevice (IR control). With nickel base alloys the corrosion is usually controlled by the anodic dissolution of the alloy, since this is normally low. This will be modelled by assuming a gradual increase in corrosion current with falling pH below the CCS value; the relationship between current and pH will be determined empirically. The influence of cathodic reaction, both oxygen reduction in natural sea water and chlorine reduction in sea water will be built into the model; the rate of reduction and the potential at which it occurs are the key factors. The influence of IR potential drops down the crevice will be included using the information on potential differences between the cathodic and anodic processes.

Phase II (1st October 1991 - 31st March 1993)

Mathematical Modelling (Task 4)

Mathematical modelling based on the mechanism developed under Task 3 is underway but at an early stage.

Crevice Corrosion Propagation Data in Natural Sea Water (Task 5.1)

This Task is due to commence in July 1992

Crevice Corrosion Propagation Data in Chlorinated Sea Water (Task 5.2)

This Task is due to commence in September 1992.

Additional Data (Task 5.3)

This task is due to commence in September 1992.

Crevice Corrosion Exposure Test Programme (Task 2.1 & 2.2)

The exposure test programme will be completed in August 1992 when information obtained on Hastelloy C22 and Hastelloy C276 will be compared with Inconel 625 data.

Verification and Use of the Mathematical Model (Task 6)

This task will commence in December 1992. The Project completion date is 31th March 1993.

J.W. Oldfield   7th Aug '92
....
J W Oldfield   7.8.92.

Table 1 Inconel Alloy 625 Samples Tested for 1 Year

Identification	Surface Finish	Assembly	Solution	Time to Initiation	Depth of Attack
IAI − 1	P	PX	SW	*−	−
IAI − 2	P	PX	SW	−	−
IAI − 5	P	PX	CL	−	−
IAI − 6	P	PX	CL	−	−
IAI − 9	P	IN	SW	21 days	TBD
IAI −10	P	IN	SW	21 days	TBD
IAI −13	P	IN	CL	21 days	TBD
IAI −14	P	IN	CL	21 days	TDB
IAI −21	G	PX	SW	−	−
IAI −22	G	PX	SW	−	−
IAI −25	G	PX	CL	−	−
IAI −26	G	PX	CL	−	−
IAI −29	G	IN	SW	−	−
IAI −30	G	IN	SW	−	−
IAI −33	G	IN	CL	−	−
IAI −34	G	IN	CL	−	−

Notes: P = Pickled, G = Ground, PX = Perspex, IN = Perspex with vinyl insert
SW = sea water, CL = Chlorinated sea water, TBD = to be determined
but les than 0.02mm.

* Represents 2 sides of each sample, upper = numbered side, lower = blank side
− indicates no initiation and no propagation

Appendix 5. Status Report : July 1993.

CORTEST
LABORATORIES LIMITED

ONR Contract N 00014-90-C-0100 Status Report at 1st July 1993

Contract Title: Development of a Mathematical Model of Crevice Corrosion Propagation on Nickel Base alloys in Natural and Chlorinated Sea Water.

Project Goals: To establish the mechanism of crevice corrosion propagation of corrosion resistant nickel base alloys in natural and chlorinated sea water. Once established the mechanism will be used to develop a mathematical model of the process to allow predictions to be made indicating under what conditions corrosion will occur and at what rate.

Present Status

The Project has been extended by 6 months and will now be completed by 30th September 1993.

Phase I (April 1st 1990- 31st September 1991)

Mechanism of Initiation of Crevice Corrosion (Tasks 1.1 & 1.2)

These tasks have been completed. It is concluded that initiation of attack in both chlorinated and unchlorinated sea water is by an acidification-depassivation mechanism. Surface finish is an influencing factor on Inconel alloy 625, a pickled surface being more prone to attack than a ground surface. The passive current appears similar on both surfaces but there are indications that in chlorinated sea water the potential on pickled material is more noble than on ground material. Crevice geometry is important, as demonstrated by exposure test results (see below).

Crevice Corrosion Exposure Test Programme (Tasks 2.1 & 2,2)

These tasks are now complete. The exposure test programme was completed during the year with a total of 48 specimens with crevice assemblies attached being tested (2 sides per specimen, 96 sides or crevices). In total 28 sides corroded, 17 in sea water, 11 in chlorinated sea water. Of the 28 sides, 26 were when a PVC insert was present giving a more severe crevice than in its absence. In terms of materials 15 sides of Hastelloy C-276 samples corroded, 12 sides of Inconel 625 and 1 side of Hastelloy C-22. Maximum depth of attack after 2 years observed on Hastelloy C-276 was .028mm on Inconel 625, .098mm and on Hastelloy C-22, .003mm.

Outline of Mathematical Model of Propagation (Task 3)

This task was completed and reported in the Status Report at 1st July 1992.

Phase II (1st October 1991 - 30th September 1993)

Mathematical Modelling (Task 4)

This is a continuing task based on the mechanism outlined in Task 3. The programme is being written in the language QBASIC.

Crevice Corrosion Propagation Data (Task 5.1 & 5.2)

Crevice corrosion propagation rates have been studied via anodic polarisation curves in very low pH aggressive environments. Maximum dissolution rates are found to be very sensitive to temperature and in view of this some of the earlier CCS determinations are being repeated, since it is felt that the temperature control may not have been accurate enough.

To help increase our understanding of the influence of solution composition, pH and temperature on the alloys being studied, various experiments were carried out.

The influence of the total chloride in the solution at a fixed pH level of zero was studied in the following solutions

1. SSW (synthetic sea water)
2. SSW with 1.5N NaCl added
3. SSW with 2.5N NaCl added
4. SSW with 5.0N NaCl added

The pH was adjusted to zero in all cases by the addition of HCl. Results are shown in Figures 1, 2 and 3. There is very little difference in the curves for any one alloy indicating very little influence of total chloride on the peak height at this pH, which is above the CCS value.

Jurinski, Scully and Lillard published a paper 'Crevice Corrosion of Alloy 625 in Chlorinated ASTM Artificial Ocean Water' (Corrosion '93, Paper 501) showing polarisation curves for Alloy 625 in HCl solutions. They used the following relationship to calculate the pH value of the solutions

$$\log \gamma \ (H+) = 0.153 \ I$$

where γ is the active coefficient for H+ and I is the ionic strength of the solution.

To study the influence of temperature on propagation, polarisation curves were obtained in a 25% concentrated HCl solution at 25°, 50° and 75°C for all 3 alloys. This solution is ~3N with a calculated pH value of ~-0.92. The results are shown in Figures 4, 5 and 6. These highlight the sensitivity of the curves and therefore the CCS values and propagation rates to temperature. One consequence of this is that

the performance of these alloys may change significantly over the temperature range 5° - 35°C, covered by natural sea water in different parts of the world. It is worth noting from these results that at 50°C the active corrosion rate of Inconel 625 in this particular solution is an order of magnitude greater than Hastelloy C-276 which is marginally greater than Hastelloy C-22.

Further studies will be carried out to determine the influence of temperature on CCS values and propagation rates.

Additional Data (Task 5.3)

To help understand the role played by alloy composition and surface finish on the initiation and propagation of crevice corrosion of the nickel base alloys ESCA and SEM/EDAX studies will be carried out to study the change, if any, in alloy composition close to the surfaces.

Verification and Use of the Mathematical Model (Task 6)

This task will commence towards the end of the Project in August 1993.
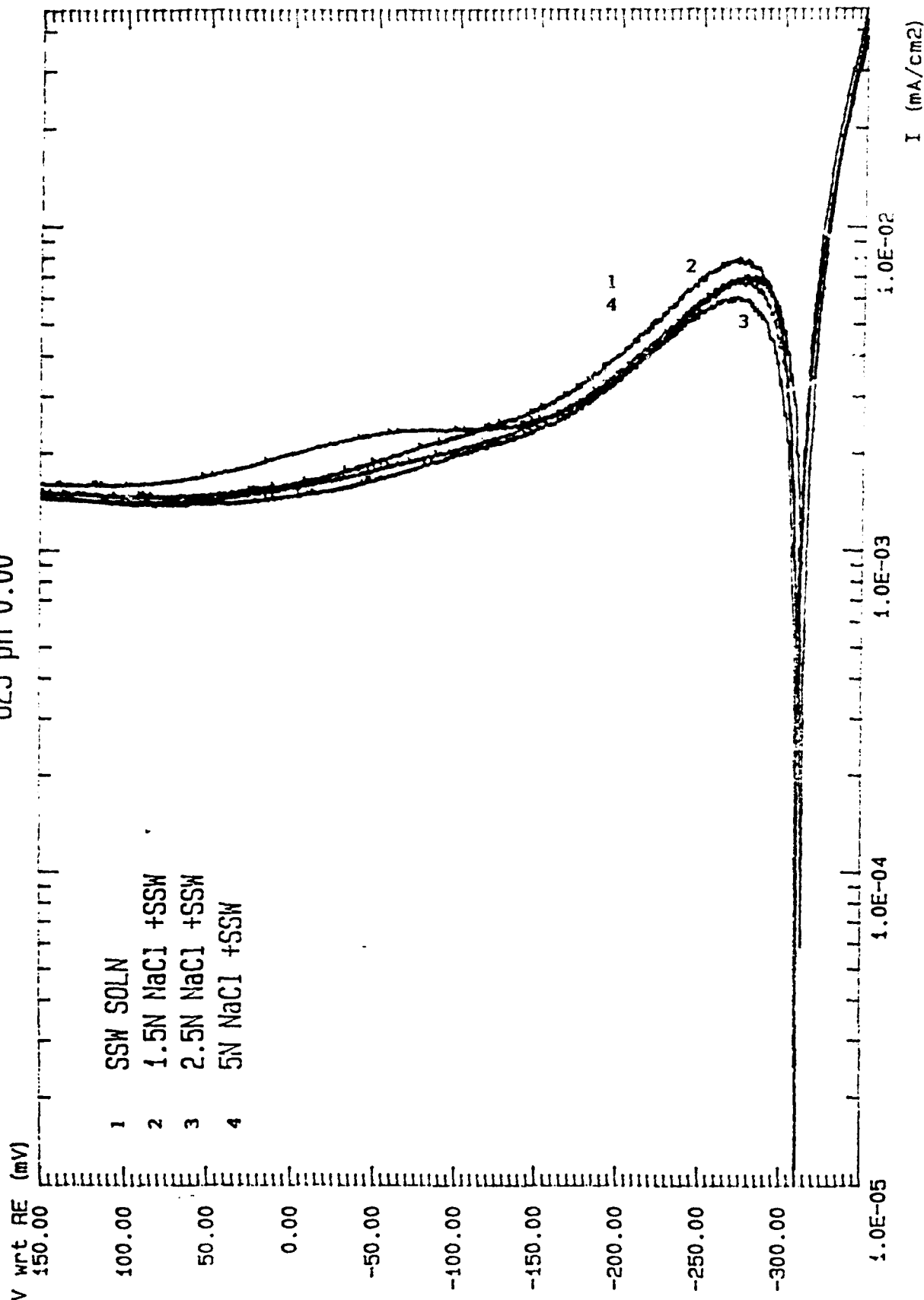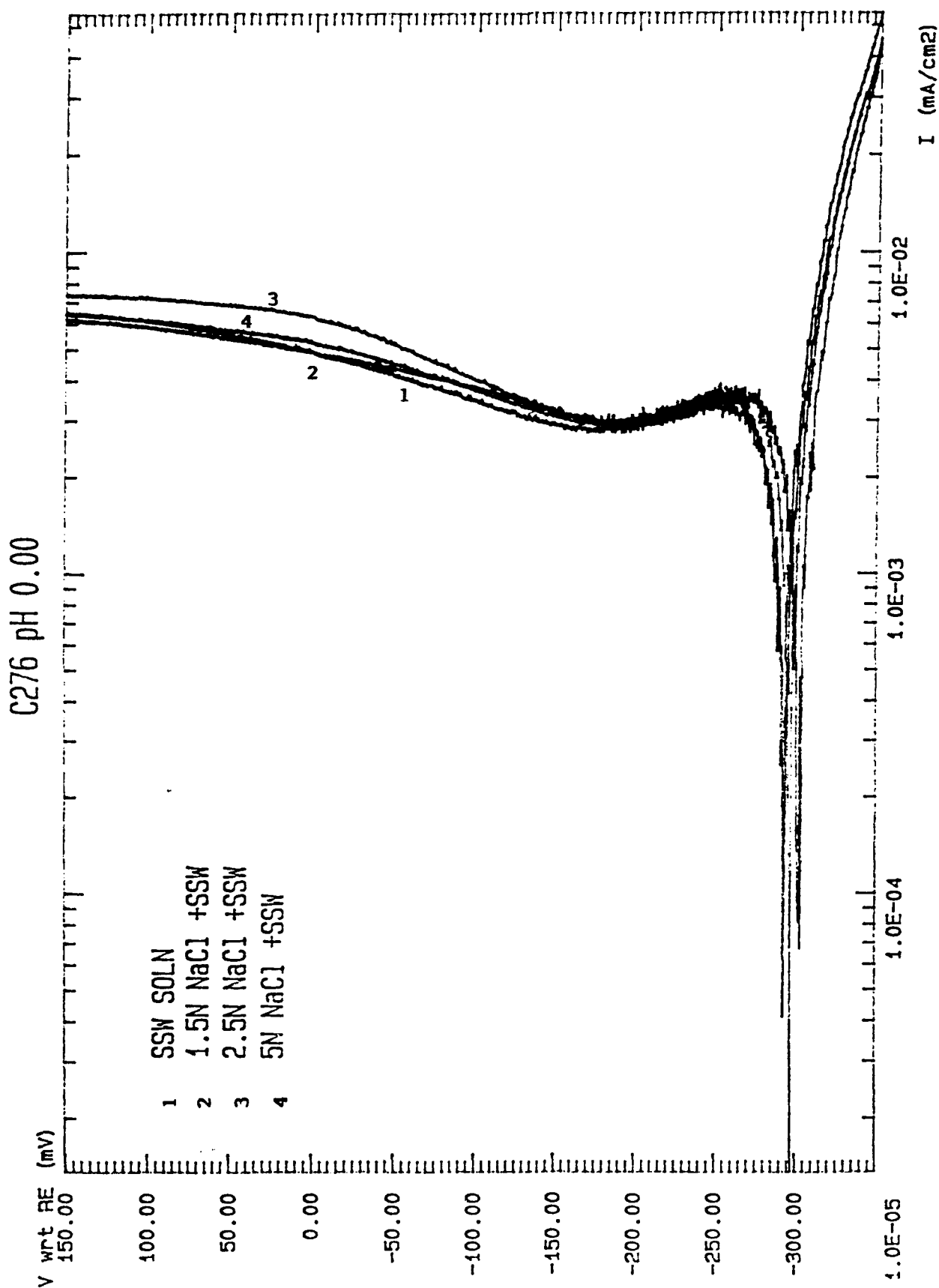
V.W. Oldku

FIGURE 1   INCONEL 625

625 pH 0.00

V wrt RE (mV)

SSW SOLN   1
1.5N NaCl +SSW   2
2.5N NaCl +SSW   3
5N NaCl +SSW   4

I (mA/cm2)

FIGURE 2   HASTELLOY C276

FIGURE 3   HASTELLOY C22

C22 pH 0.00

V wrt RE (mV)

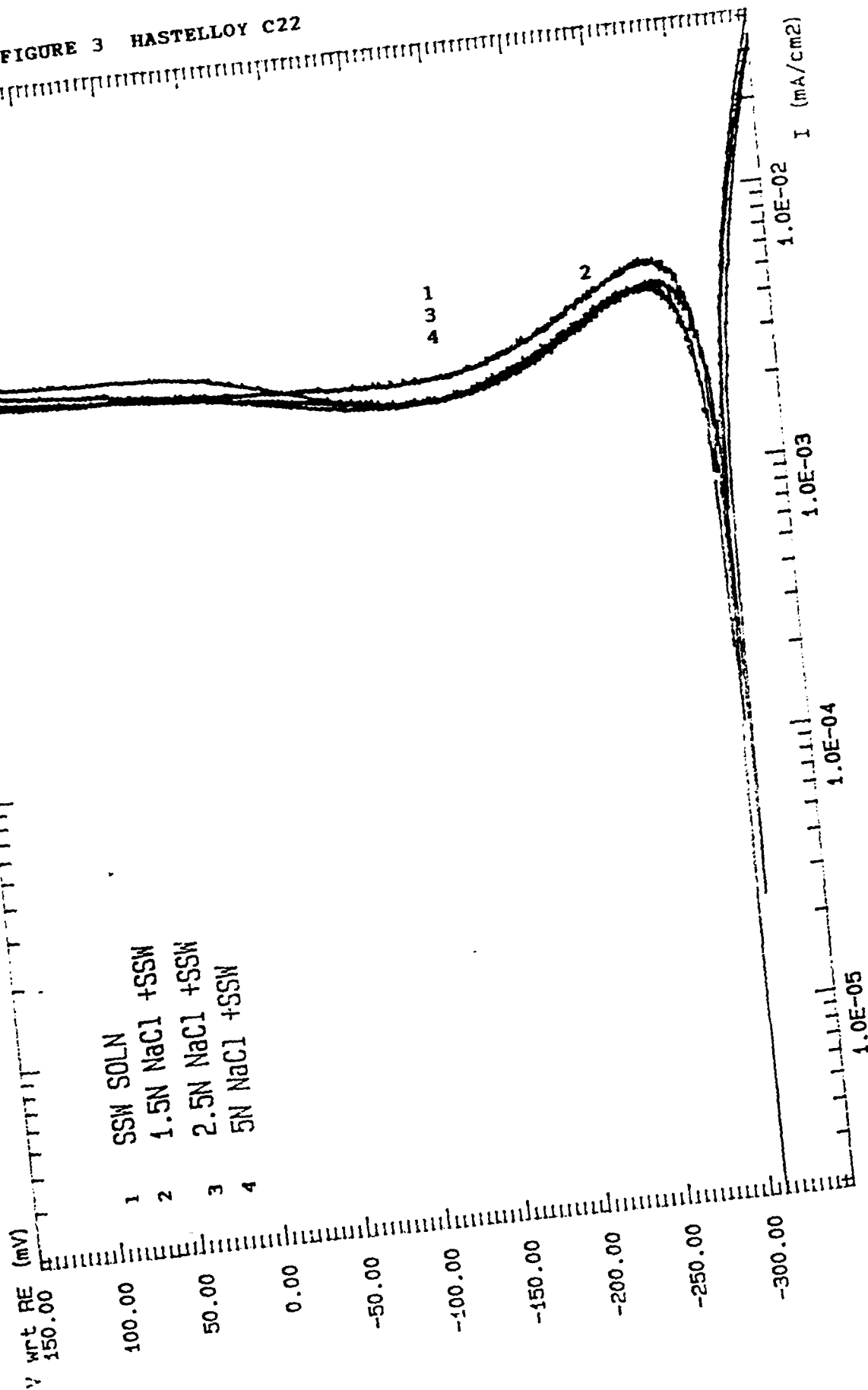|	SSW SOLN
1	SSW SOLN
2	1.5N NaCl +SSW
3	2.5N NaCl +SSW
4	5N NaCl +SSW

I (mA/cm2)
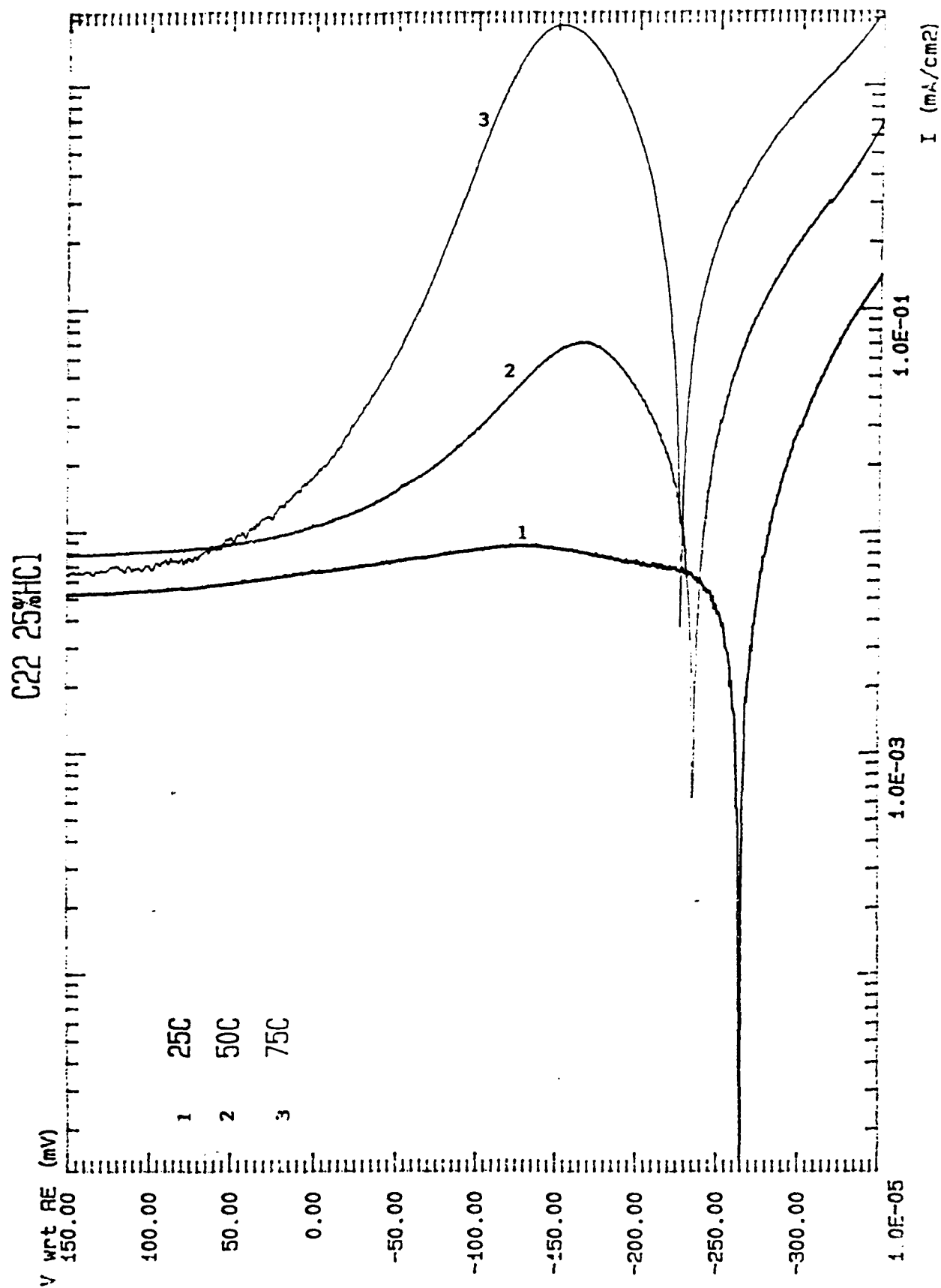
FIGURE 4   INCONEL 625
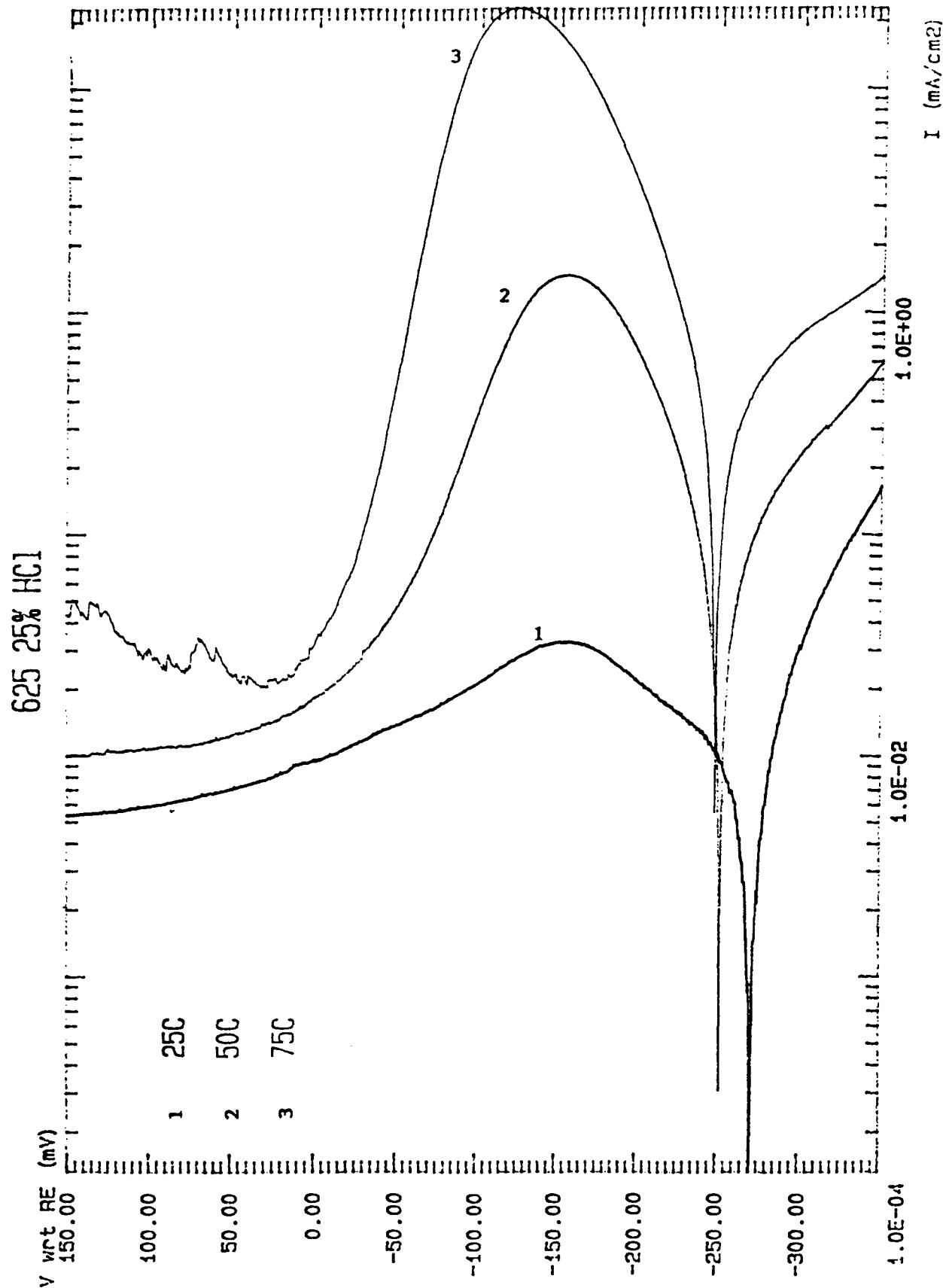
FIGURE 5   HASTELLOY C276
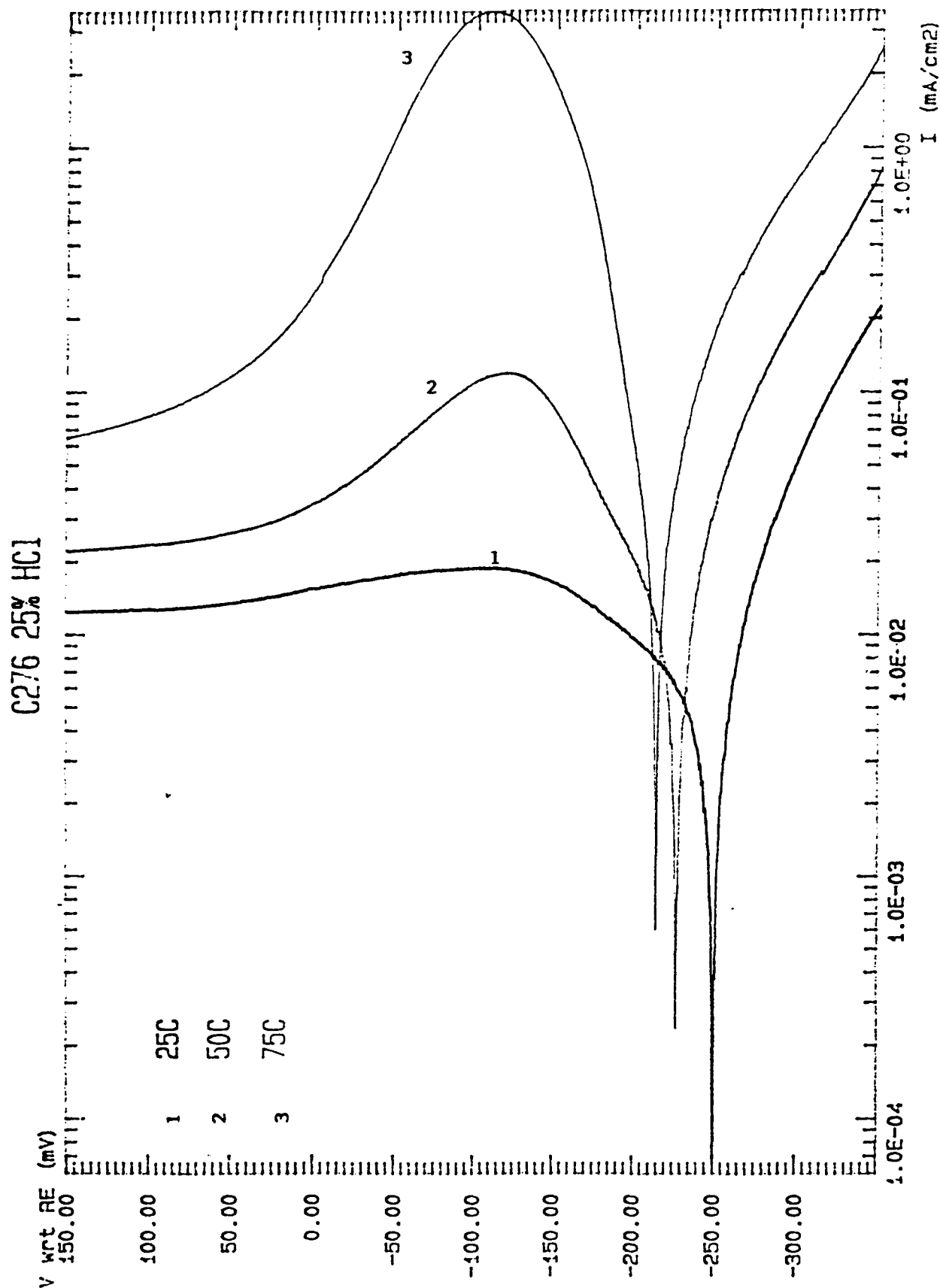
FIGURE 6   HASTELLOY C22

Appendix 6. Paper 'Performance of Nickel Base Alloys
in Critical Sea Water Applications' by
J W Oldfield. NACE Corrosion Asia '94,
Singapore 26-30th September 1994.

Performance of Nickel Base Alloys in Critical Sea Water Applications

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Abstract

Nickel base alloys such as Alloy 625, C22 and C276 are generally considered to have exceptional corrosion resistance in critical sea water applications at ambient temperature. Test results published in recent years however indicate that severe crevice corrosion of some of these alloys may occur under certain conditions. Exposure tests have been carried out in natural and chlorinated sea water, together with electrochemical studies and simple mathematical modelling. These data help to explain the observed phenomena and go some way to allowing the safe selection of nickel base alloys for critical sea water application.

Key terms: crevice corrosion, sea water, nickel base alloys,mathematical modelling

Introduction

Corrosion resistant nickel base alloys have for many years been considered excellent materials for use in natural and chlorinated sea water; their pitting and crevice corrosion resistance in particular has been accepted as being good enough for the majority of applications. However, more recently some sea water exposure tests [1,2] have shown initiation of attack and in some cases unexpectedly high rates of propagation of attack have been observed. The results presented here are part of a fundamental program of work, sponsored by ONR, aimed at establishing the mechanism of crevice corrosion propagation of these alloys, this to be used to develop a mathematical model of the process to allow predictions to be made indicating under what conditions corrosion will occur and at what rate. Data are reported from exposure tests in natural and chlorinated sea water, electrochemical studies, simple mathematical modelling and some surface analysis. Results confirm the strong influence of crevice geometry on the initiation of attack and indicate that temperature variations observed in sea water around the world could well account for marked differences in propagation rates.

Background

Mechanism of Crevice Corrosion in Natural Sea Water
The successful use of stainless steels and nickel base alloys in sea water depends to a large extent on their resistance to crevice corrosion. This form of attack typically occurs in shielded areas in bulk environments containing chloride ions. The mechanism of crevice corrosion which is now generally accepted [3] can be outlined as a four stage process.

Firstly the solution within the crevice becomes deoxygenated as a result of the passive current flowing in the occluded area; the rate of oxygen diffusion into the crevice is not rapid enough to replace its rate of depletion as the cathode process matches the anodic current. Once this has occurred the cathodic process moves outside the crevice and the anode and cathode are now separated. Current flows between the two and mass transport phenomena result in a build-up of chloride ions and a reduction in pH within the crevice. This second stage continues until either a steady state is reached with no corrosion occurring or the crevice solution reaches a composition which, combined with the potential distribution in the crevice causes breakdown of the passive film on the alloy. Once breakdown has occurred (stage 3) the final stage, propagation of attack commences.

It should be noted that various detailed mechanisms have been put forward for the actual breakdown stage of crevice corrosion (4,5.). However, in general these result in the potential within the crevice being on a part of the polarisation curve for the alloy in the crevice solution such that corrosion will initiate. This can be either in a 'pitting region' or in an 'active region'. The current which is referred to as the 'passive current' can be either a uniform, low passive current over the entire surface of the alloy or a relatively high current at local defects. Solution changes that occur can also be local within the crevice resulting from dissolution of inclusions (6). This breakdown mechanism differs from that described above but has been shown to be possible on 304 stainless steel containing MnS inclusion.

Once breakdown has occurred propagation of attack proceeds and is controlled by the anodic or cathodic process or the 'IR' potential drop down the crevice between the anode and the cathode. This process is dynamic and in many cases controlling factors change as the process progresses e.g. attack may commence deep inside the crevice under IR control; the corroding area will then move towards the mouth of the crevice where anodic or cathodic control takes over.

Mathematical Modelling of Crevice Corrosion in Natural Sea Water
The first attempt at developing a mathematical model of crevice corrosion of stainless steels and nickel base alloys in sea water was published in 1978 (7). This simple model was successful in that it quantified the mechanism of initiation of attack, using appropriate input parameters, in particular critical crevice solution values (i.e. that solution which will break down the passive film) and passive current values. Predictions of this model were quite accurate in terms whether or not corrosion would occur and if so how long the initiation period would be. Since 1978 a number of models have been developed which are significantly more rigorous than the earlier one (e.g. 8,9). Other studies, on 304 stainless steel in particular, indicate that a different mechanism of breakdown occurs and this has also been modelled (10).

To assist with the further development of crevice corrosion modelling relating specifically to nickel base alloys, and particularly to propagation, additional practical information is required. This paper reports experiments to obtain that data, leading to an explanation of high corrosion propagation rates observed for Alloy 625 under certain conditions (1).

Experimental

Materials

Three nickel base alloys were tested in this study Inconel* 625 (UNS No. N06625), Hastelloy* C22 (UNS No. N26022) and Hastelloy* C276 (UNS No. N10276). The Inconel alloy was supplied by Inco, the Hastelloy alloys were supplied by Haynes International. The compositions from the manufacturers certificates are given in Table 1. Alloy 625 was supplied in the pickled condition, the Alloys C22 and C276 in the cold rolled and annealed condition. All materials were in the form of ~3mm sheet.

Exposure Tests

Crevice corrosion exposure tests were carried out at the UK's Defence Research Agency facility, on hire to Cortest, at Holton Heath, Poole, UK. Stored sea water was available in the laboratory for use on a once through basis.

Tests were carried out in two environments, natural and chlorinated once through sea water. Chlorination was achieved by adding sodium hypochlorite in a mixing tank which fed into the exposure tank. The residual chlorine level was maintained at nominally 1ppm by regular measurement and subsequent adjustment to the mixing tank. Temperature was ambient, flow rate in both tanks was 11 litre/h and each tank had a capacity of ~120 litres.

Samples were 100 X 75mm in size (and ~3mm thick) with a 15mm diameter hole in the centre. Two surface finishes were used for each alloy, the 'as received' surface (pickled for Alloy 625, cold rolled and annealed for Alloys C22 and C276) and a ground surface. The ground surfaces were applied by the manufacturers. These surfaces were characterised by Talisurf measurement of surface roughness and these are reported in Table 2.

The crevice assembly used was the Perspex* crevice assembly described in detail elsewhere (11). Essentially it consists of two crevice formers , each with a 5mm circular annulus and approximately 30mm diameter fastened through the central hole in the specimen by means of a nut and bolt, torqued up wet to 10Nm. Two crevice geometries were considered, one as just described a second with a 0.2mm thick PVC annular ring between the Perspex and the metal, this giving a tighter and therefore more severe crevice.

Under each set of conditions duplicate samples of each alloy were tested for a 2 year duration. For Alloy 625 an additional set of specimens were tested and removed after 1 year. The test parameters are summarised in Table 3.

During the exposure tests in situ visual observations were made daily for evidence of corrosion for the first month; this was then reduced to weekly examination.

* Trademark

Electrochemical Studies

Electrochemical studies were carried out to determine the critical crevice solution (CCS) of each alloy over a range of temperatures. The method used is described elsewhere(4) but involves obtaining a series of polarisation curves in increasingly aggressive solutions (high chloride, low pH) to simulate the development of a solution in the crevice. The CCS is that solution which will give an anodic active peak height of $10\mu a/cm^2$. The CCS is thereby a solution which can cause breakdown of the protective passive film within a crevice. For comparative purposes CCS values obtained in HCl solutions alone were also determined.

Surface Analysis

To examine possible depletion of alloying elements close to the surface SEM/EDAX analysis was carried out over the first $20\mu m$ from the outer surface of each surface finish on each of the three alloys.

Results

Exposure Tests

Environmental conditions over the period of the exposure tests are given in Table 4. A summary of the observed results for the initiation of attack are shown in Tables 5 and 6. Times to initiation are not given since the visual observations made during the test are not considered totally accurate. However, an indication of actual times to breakdown is given in Table 7; these show that breakdown occurs early in the exposure test. Maximum depths of attack are given in Tables 8 and 9 for metal/PVC and metal/Perspex crevices respectively. It should be noted that the area of attack on the one sample of Alloy C22 which showed corrosion was an extremely small pit at the edge of the crevice, the same applies to the pickled sample of Alloy 625 which corroded under the Perspex crevice. The corroded area of the ground sample of Alloy 625 under the Perspex crevice was small but significant. The corroded area under all the other samples which initiated was much greater, approaching the entire crevice area.

Electrochemical Studies

CCS values were obtained over a range of temperatures for the three alloys being studied using the conventional technique described elsewhere (4). Results are shown in Table 10 and compared with values obtained in HCl solutions alone as described by Jurinski et al (12)

Mathematical Modelling

The CCS values given in Table 10 have been used as input to Cortest's mathematical model of crevice corrosion (7). Alloy compositions given in Table 1 were used as input, together with a passive current value of $0.1\mu A/cm^2$. The model was run in the mode described previously (4) and used in other publications by the author (13). Results are shown graphically in Figure 1. The crevice corrosion resistance is the time it would take for a $1\mu m$ metal to non-metal crevice to break down in hours under hypothetical conditions that no diffusion out of the crevice can occur. In other words no steady state can develop and therefore breakdown must eventually occur.

Surface Analysis

The variation of the levels of Cr, Ni and Mo close to the surface of the three alloys under study in each of their two surface conditions is of most interest. These are shown in Figure 2, 3 and 4 respectively.

Discussion

Notwithstanding the difficulties of obtaining reproducible results in crevice corrosion testing the exposure tests reported here allow a number of conclusions to be drawn. These are summarised below:-

- when initiation does occur it is within a relatively short time e.g. weeks
- in terms of resistance to initiation of attack Alloy C22 performed the best followed by Alloy 625 with Alloy C276 showing the greatest number of initiated sites
- surface finish effects were mixed, on Alloy 625 the pickled surface showed much greater tendency to initiate than the ground surface, on Alloy C276 both the CR annealed and the ground surface were susceptible. On Alloy C22 there was essentially no corrosion and therefore no effect
- crevice geometry effects very clearly showed the PVC-metal crevice to be much more severe that the Perspex metal crevice
- in terms of initiation there was little difference between sea water and chlorinated sea water.
- in terms of propagation on Alloy 625 the corrosion rate was less in chlorinated sea water than sea water alone. Maximum depths of attack at 2 years were significantly greater than at 1 year. All corrosion was on a pickled surface
- in terms of propagation on Alloy C276 the corrosion rate on a ground surface was less than on the CR annealed surface. Depths of attack were slightly less in chlorinated sea water on the CR annealed surface but the same on the ground surface.

The model predictions of resistance to initiation of attack show agreement in the relative performance of Alloy 625 and Alloy C22 at around ambient temperature. Alloy C276 is ranked to perform better than it actually did. According to the US Navy data base (14) the material has outperformed Alloy 625 in many exposure tests, in agreement with the present model predictions. The explanation for this lies in the variation in surface roughness and in alloy composition close to the surface compared with in the bulk, illustrated in Figures 2,3 and 4. The significance of the alloy composition variations can be seen by using these to calculate pitting resistance equivalent numbers (PRE's) based on the formula Cr + 3Mo for the surface and bulk of each alloy in each surface condition. These results are shown in Table 11. This indicates Alloy C22 to be the best material in both surface conditions, it also shows that pickled Alloy 625 is inferior to the ground surface, confirming what was found in the exposure tests. Again based on the PRE numbers Alloy C276 is predicted to be superior to ground Alloy 625 and would therefore not be expected to corrode.

The crevice severity is a function of the surface roughness, the smaller the roughness the greater the severity. Referring to Table 2 we see that the Alloy C276

crevices were therefore much more severe than the Alloy 625 ones. This is considered to be the reason why this alloy corroded. In other words the exposure test was not comparing like with like, had the surface roughness on Alloy C276 been the same as on Alloy 625 it would probably not have corroded.

Thus surface composition considerations and surface roughness effects allow a full explanation of the exposure test results of initiation of corrosion; their compatibility with model ranking predictions is also confirmed.

Turning now to propagation of crevice corrosion, if the corrosion rate is controlled by the anodic dissolution of the alloy then it is the initial crevice geometry and the temperature which will determine this rate. As geometry becomes more severe (i.e. tighter, deeper crevices) a more aggressive, lower pH can develop which equates to a higher alloy dissolution rate. As the temperature increases, again the active dissolution rate increases. These effects are illustrated in Figure 5 and 6. The maximum depth of attack data reported in Table 8 can be converted to an anodic current using the approximate relationship that $1\mu A/cm^2$ is equivalent to a corrosion rate of 0.01mm/year. The corrosion rate for Alloy 625 then corresponds to a current of 6.2 and $3.0\mu A/cm^2$ in sea water and chlorinated sea water in 1 year tests. The currents for Alloy C276 are lower and in the range $0.8 - 1.4\mu A/cm^2$.

The data in Figure 5 and 6 was obtained dynamically. Steady state measurements will reduce the current values somewhat but nevertheless it is clear that small changes in the combination of pH i.e. crevice severity, and temperature can result in large changes in corrosion rate. For example, if we assume that steady state current values are a factor of 5 less than the dynamic ones in Figure 5 and 6, and that the observed temperature variations at pH -0.94 is similar at other pH values then maximum corrosion rates can be estimated for given crevice solution pH values and temperature. Examples are shown in Table 12 for solution pH values of -0.94 and -1.21 with temperatures of 15°C and 30°C respectively for Alloys 625 and C276. The change in corrosion rate for Alloy 625 is greater than a hundredfold for these relatively small changes in condition. Such changes have been seen in practice (1) and this mechanism is put forward to explain them. Note that the temperature range chosen for the example is within the range of variation of natural sea water; the pH values chosen are considered sensible for severe and very severe crevices.

Thus although the exposure test data on propagation rates is limited, when coupled with other data (1) and the electrochemical studies, a mechanism that predicts and explains large differences in corrosion rates on Alloy 625, which have been observed, has been put forward.

Summary and Conclusions

Crevice corrosion initiation and propagation of nickel base alloys Alloy 625, Alloy C276 and Alloy C22 in sea water and chlorinated sea water has been studied by exposure tests, electrochemical studies, surface analysis and mathematical modelling. The initiation of attack has been shown to be a function of crevice geometry and surface composition and has been successfully predicted by the modelling route. A mechanism of propagation has been suggested which

successfully predicts large differences in the corrosion rate of Alloy 625 for relatively small changes in crevice geometry and temperature.

Acknowledgement

References

1.   R.M. Kain, R.J. Ferrara, B. Shaw CORROSION/89, Paper no. 112, (Houston, TX: National Association of Corrosion Engineers, 1989).

2.   E.D Thomas, K.E. Lucas, M.H. Peterson, D.K. Christian, CORROSION/88, Paper no. 402, (Houston, TX: National Association of Corrosion Engineers, 1988).

3.   M.G. Fontana, N.D. Green, Corrosion Engineering (McGraw Hill, New York 1967) p.41.

4.   J.W. Oldfield, W.H. Sutton, Br. Corros. J. 15 (1980), p.31.

5.   H.W. Pickering, Corros. Sci. 29 (1989), p.325.

6.   S.E. Lott, R.C. Alkire, J. Electrochem. Soc. 136 (1989), p.973.

7.   J.W. Oldfield, W.H. Sutton, Br. Corros. J. 13 (1987), p.13.

8.   M.K. Watson, J. Postlethwaite, CORROSION/90, Paper no. 156. (Houston, TX: National Association of Corrosion Engineers, 1990).

9.   P.O. Gartland 12th International Corrosion Congress, Vol. 3B, p.1901, (Houston, TX: National Association of Corrosion Engineers, 1993).

10. R.C. Alkire, S.E. Lott, J. Electrochem. Soc. 136 (1989), p. 3256.

11. J.W. Oldfield, Internation Materials Review, 32 (1987), No.3.

12. M.P. Jurinski, J.R. Scully, R.S. Lillard, CORROSION/93, Paper no. 501, (Houston, TX: National Association of Corrosion Engineers, 1993).

13. J.W. Oldfield, CORROSION/88, Paper no. 409, (Houston, TX: National Association of Corrosion Engineers, 1988).

14. A.J. Sedriks, ONR, Arlington, Virginia - Private Communication, 1991.

Table 1 Chemical Composition of Alloys Studied

Alloy	Composition %									
	C	Cr	Mo	Ni	Fe	S	Al	Ti	Nb +Ta	W
Alloy 625	0.03	22.33	8.82	60.04	4.47	<0.001	0.23	0.21	3.55	-
Alloy C22	0.003	21.4	13.9	bal	4.2	<0.002	-	-	-	2.9
Alloy C276	0.003	15.44	15.96	bal	5.39	0.002	-	-	-	3.21

Table 2 Surface Roughness of Alloys Tested

Alloy	Surface Finish	Surface Roughness (Ra value , µm)
Alloy 625	Pickled	1.61
	Ground	1.90
Alloy C22	CR and Annealed	0.20
	Ground	0.46
Alloy C276	CR and Annealed	0.22
	Ground	0.47

Table 3 Expoure Test Parameters

Environment	- natural and chlorinated (1ppm) sea water
Materials	- Alloy 625, Alloy C22, Alloy C276
Surface Finish	- As received and ground
Crevice Geometry	- 5mm annulus Perspex crevice with and without PVC insert
Test Duration	- 2 years for all alloys, 1 year also for Alloy 625
Samples	- Duplicates

Note: Total number of samples: Alloy 625 - 32, Alloy C22 -16, Alloy C276 -16

Table 4 Environmental Conditions over the Period of the Exposure Tests

Environment	Temperature Range	Average	Residual Chlorine Range	Average	pH Range
Sea water	15.0-22.5	17.6		-	7.91-8.11
Chlorinated sea water	15.0-22.5	18.0	2.0-0.+	1.14	7.83-8.17

Table 5 Initiation of Crevice Corrosion in Natural Sea Water Tests

Crevice Geometry	Alloy	Surface Finish	Crevice* Initiated	Total no. of Samples
Perspex/Metal	Alloy 625	Pickled	1/8	4
		Ground	1/8	4
	Alloy C22	CR Annealed	0/4	2
		Ground	0/4	2
	Alloy C276	CR Annealed	0/4	2
		Ground	0/4	2
PVC/Metal	Alloy 625	Pickled	6/8	4
		Ground	0/8	4
	Alloy C22	CR Annealed	1/4	2
		Ground	0/4	2
	Alloy C276	CR Annealed	4/4	2
		Ground	4/4	2

* There are two crevices per assembly; results are reported as crevices initiated/total number of crevices

Table 6 Initiation of Crevice Corrosion in Chlorinated Sea Water Tests

Crevice Geometry	Alloy	Surface Finish	Crevice Initiated	Total no. of Samples
Perspex/Metal	Alloy 625	Pickled	0/8	4
		Ground	0/8	4
	Alloy C22	CR Annealed	0/4	2
		Ground	0/4	2
	Alloy C276	CR Annealed	0/4	2
		Ground	0/4	2
PVC/Metal	Alloy 625	Pickled	4/8	4
		Ground	0/8	4
	Alloy C22	CR Annealed	0/4	2
		Ground	0/4	2
	Alloy C276	CR Annealed	4/4	2
		Ground	3/4	2

Table 7 Comparison of Observed Corrosion on Completion of Test and Times
to Initiation Noted During Test

Alloy	Total sides corroded	Visual observation during test
Alloy 625	12/48	10 at 21 days 1 at 68 days 1 not observed visually
Alloy C22	1/32	1 not observed visually
Alloy C276	15/32	13 at 21 days 1 at 162 days 1 not observed visually

Table 8 Maximum Depth of Attack on Corroded Samples
with Metal/PVC Crevice

Alloy	Surface	Maximum Depth of Attack (mm)
Alloy 625	Pickled 1 yr tests sea water	.062
	2 yr test sea water	.098
	1 yr test Cl_2 sea water	.030
	2 yr test Cl_2 sea water	.076
Alloy C22	CR Annealed 2yr test sea water	.003
Alloy C276	CR Annealed 2 yr test sea water	.028
	2 yr test Cl_2 sea water	.021
	Ground 2 yr test sea water	.015
	2 yr test Cl_2 sea water	.016

Table 9 Depth of Attack on Corroded Samples with Metal/Perspex Crevices

Alloy	Surface	Maximum Depth of Attack (mm)
Alloy 625	Pickled 2 yr tests sea water	<.0016
	Ground 2 yr test sea water	.019

Table 10 Critical Crevice Solution Values Defined as a pH Value

Temperature	Alloy		
	Alloy 625	Alloy C276	Alloy C22
5	-0.60	NA	NA
20	-0.32	NA	NA
25*	-0.20	-0.62	-0.95
30	~0.27	-0.37	<-1.0
50		0.00	0.04
73	0.76	0.34	0.54

* Values obtained in HCl solutions alone. pH calculated
according to reference 12.
NA: No CCS values obtained, $10 \mu A/cm^2$ not achieved on
active peak.

Table 11 Pitting Resistance Equivalents (PRE) of Alloys

Alloy	Surface Condition	PRE (surface)	PRE (bulk)
Alloy 625	Pickled	48.8	48.8
	Ground	56.4	48.8
Alloy C276	CR Annealed	62.2	63.3
	Ground	63.8	63.3
Alloy C22	CR Annealed	68.9	63.1
	Ground	64.3	63.1

Table 12 Maximum Calculated Propagation rates under various conditions

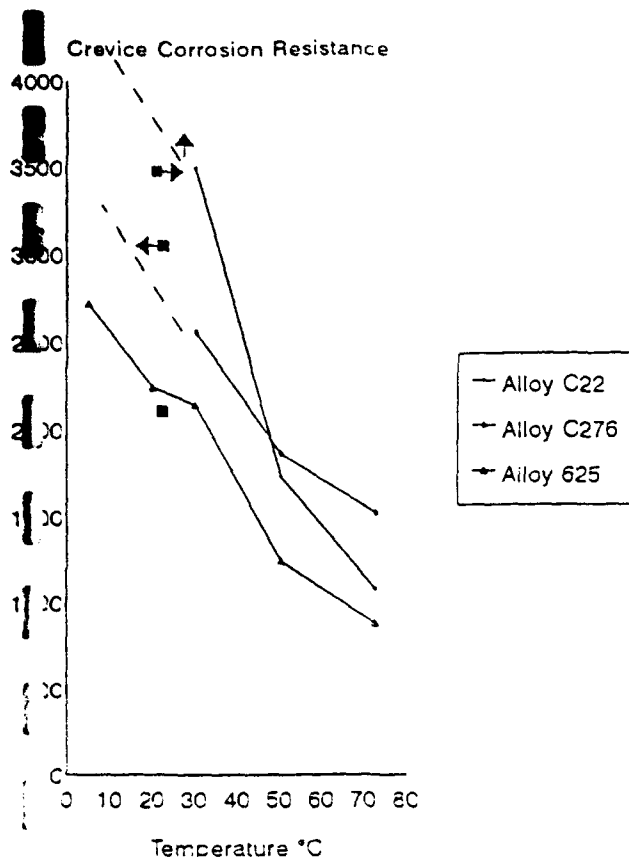| Alloy	Crevice solution pH	Temperature	Current Density ($\mu A/cm^2$)	Approximate Corrosion Rate (mm/y)
Alloy 625	-0.94	15*	2.0	.02
	-1.21	30*	277	2.77
Alloy C276	-0.94	15*	1.2	.01
	-1.21	30*	15.5	.16

Figure 1. Crevice Corrosion Resistance as a Function of Temperature.
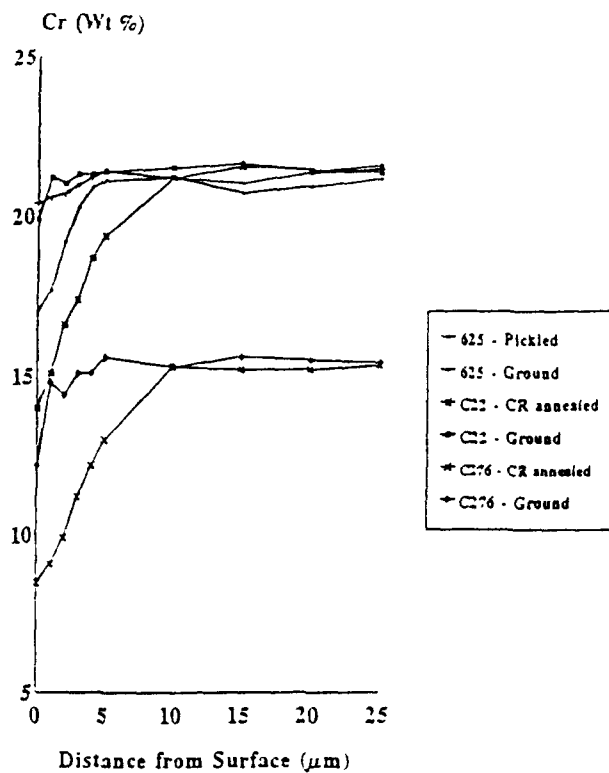(■ Data Based on HCl CCS Determination)

Figure 2. Variation in Cr content close to the surface as a function of alloy and condition.
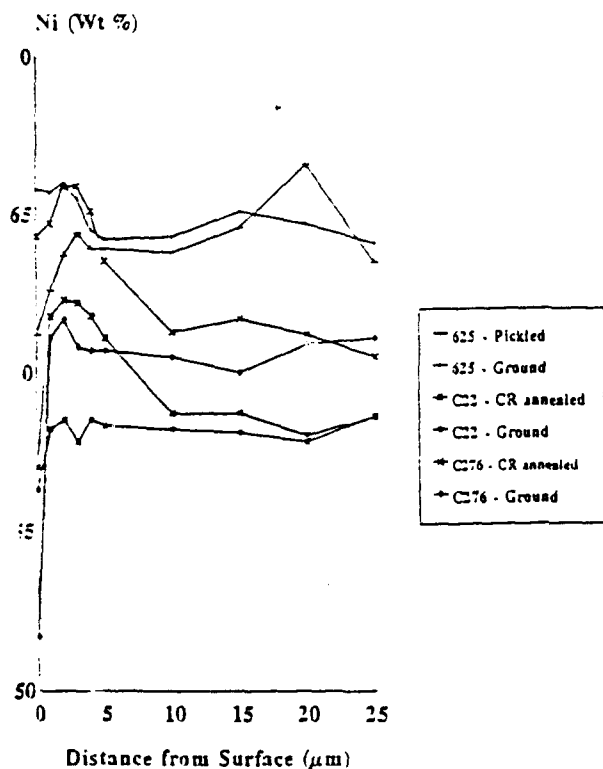

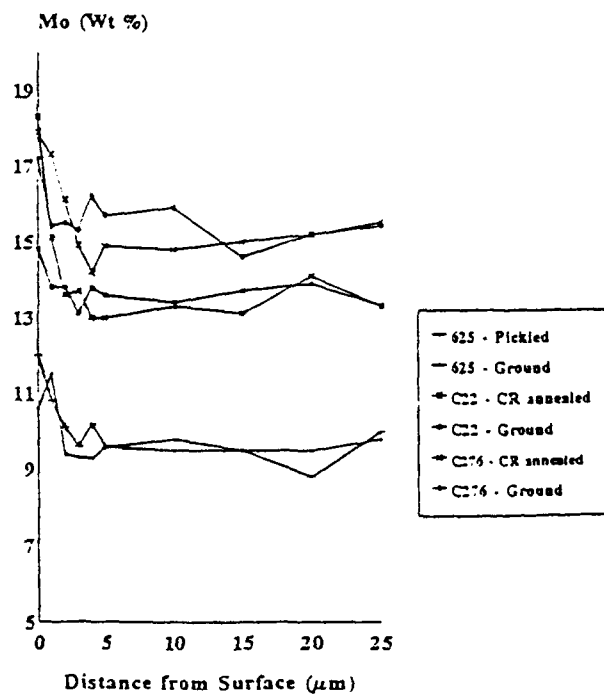Figure 3. Variation in Ni content close to the surface as a function of alloy and condition.

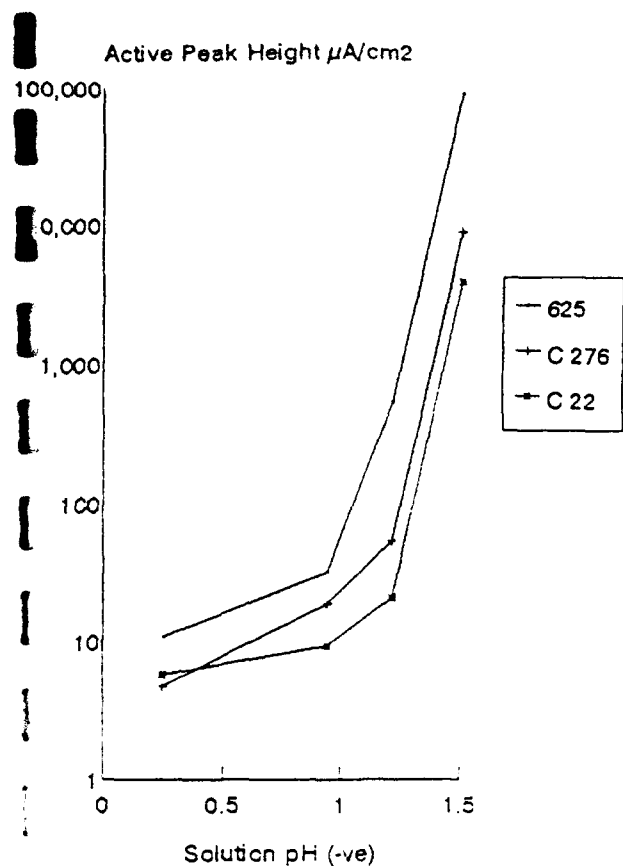Figure 4. Variation in Mo content close to the surface as a function of alloy and condition.

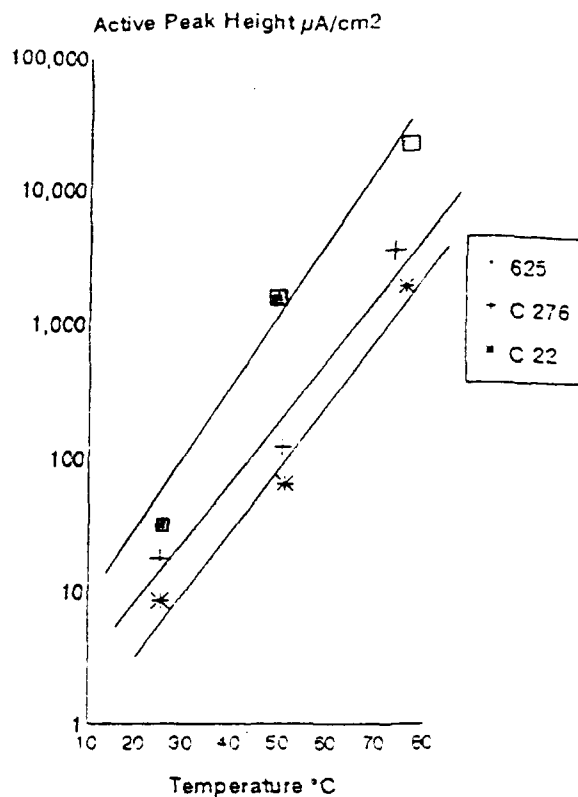Figure 5. Effect of pH of an HCl Solution on the Anodic Active Peak Height at 25 °C.

Figure 6. Effect of Temperature on the Anodic Active Peak Height in 25% HCl solution of pH -0.94.